



ELECTROCHEMICAL STUDIES ON BIOLOGICAL AND MODEL MEMBRANES

THESIS

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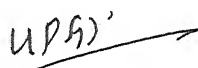
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Certificate

This is to certify that the thesis entitled "Electrochemical Studies on Biological and Model Membranes" being submitted to the Bundelkhand University, Jhansi, for the award of the degree of "Doctor of Science" in Chemistry, is a record of bonafied research work carried out by Dr. Mohd. Ayub Ansari at Membrane Research Laboratory, Department of Chemistry, Bipin Bihari (PG) Science College, Jhansi. (UP).


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Declaration

I hereby declare that the thesis entitled "Electrochemical Studies on Biological and Model Membranes" being submitted for the degree of "Doctor of Science" to the Bundelkhand University, Jhansi, is an innovative piece of work which has been carried out by me at Membrane Research Laboratory, Department of Chemistry, Bipin Bihari (PG) Science College, Jhansi. (UP).

To the best of my knowledge and belief it has not been submitted in part or full for any other degree.

Jhansi : October, 2005

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Chapter-I

Introduction

In nature the difference between relatively simple organisms such as bacteria and complex organisms with many cells such as insects, plants and animals is the creative use of membranes to separate chemical processes. In science, the application of membrane technologies frequently allows research programmes to evolve to higher levels. In society, membranes allow many communities to benefit from things as varied as clear apple juice, clean water and kidney machines to more cost effective, safer, pharmaceuticals.

The word membrane comes from Latin word, "membrana" that means skin¹. Today's word "membrane" has been extended to describe a thin flexible sheet or film, acting as a selective boundary between two phases because of its semi permeable properties. Physically a membrane could be solid or liquid. Its function is as a separation agent that very selective based on the difference of diffusivity coefficient, electric current or solubility.

A precise and complete definition of the membrane is difficult to make and any complete definition given to cover all the facts of membrane behaviour will be incomplete. According to Sollner² "A membrane is a phase or structure interposed between two phases or compartments which obstructs or completely prevents gross mass movement between the latter, but permits passage, with various degrees of restriction of one or several species of particles from the one to the other or between the two adjacent phases or compartments, and which thereby acting as a physicochemical machine transforms with various degrees of efficiency according to its nature and the nature and composition of the two adjacent phases or compartments." Actually membrane has become an integral part of our daily lives. All cells comprising living things, are surrounded by

membrane. Biological membranes (membrane cells) are very selective that transfer only particular species.

Transport phenomena in membrane has acquired considerable significance during the last few decades because of its direct impact in desalination, ion sensor techniques, fuel cell technology nanotechnology, electrical storage batteries, medicine and several other processes. The investigators from various disciplines e.g. chemists, chemical engineers, physicists and biologists have contributed extensively, although the aims and the starting points have been quite different. The literature in this field is enormous but not very coherent

The number of recent published research papers³⁻⁶ and reviews⁷⁻¹² and books¹³⁻¹⁶ has witnessed a rapid growth in the development and use of model membranes for carrying out investigations of various aspects of bio-electric phenomena. A number of investigators have developed simple, well defined and stable model membranes,¹⁷⁻²¹ lipid bilayer membrane have been considered as the most realistic model except for few shortcomings. Parchment paper, which mimic some of the functional properties of electrolyte cell and gastric mucosal membranes, have been used to study the rectification phenomena in biological systems and in some other physico-chemical studies. Inorganic precipitate membranes, owing to their stability at higher temperatures, ion exchange power and strong adsorption characteristics have been used in many processes of nuclear and chemical technology and electrosynthesis of organic compounds in some non conducting media.

Many of the processes occurring in nature involve membrane transport. Some of the functions performed by such membranes appear to be unique, as well as efficient and it could be possible to prepare synthetic membrane of similar properties. Furthermore, knowledge of synthetic membranes with a view to understand the changes which occur in biological ones is the main interest of the

authors. However, the main object is the examination of the extent to which electroanalytical method may be applied to answer the questions concerning the physical chemistry of ion transport across membranes.

Model and biological membranes are studied simultaneously by using the recently developed theories. Biological membranes with the exception of cell membranes, are thin sheets of tissue that cover various organs of body and plants. Of the hundreds of biological membranes, one of the more familiar is the mucous membrane. The mucous membrane functions as a barrier to keep toxic components contacting one side of the membrane from tissue on the other side but allows transport of species essential for that tissue. Model or synthetic membranes are sub-classified by composition, function, structure and form. Composition refers to the material used to make the membrane i.e., organic or inorganic polymer. Functional classification of membranes includes gas separation, water desalination, dialysis etc. Form denotes whether the membrane is a film hollow fiber tube, or coating.

Model (synthetic) membranes because of their stability in various environment situations have quite often been utilized as a model for the studies of transport phenomena. Beg and co-workers²²⁻²⁵ have in a series of papers reported the preparation of various types of membranes using inorganic precipitates and supporters/binders and have utilized them as model to study the mechanism of transport of ions as well as to the validity of some recently developed equations for membrane potential.

From a view of the membrane phenomena over the long time span of about fifty years the science of membrane permeability has undergone a remarkable development with the arrival of the new concept of irreversible thermodynamics. Kobatake et al.^{26,27} and Nagasawa et al.²⁸ developed a certain theories of membrane potential based on non equilibrium thermodynamics for synthetic

membranes such as ion-exchange membranes (IEM) and bilayer lipid membrane (BLM) etc. prepared in laboratories using various chemical substances. The transport of ions across these artificial membranes is a passive phenomena and is governed by physical forces. This phenomena is followed by the irreversible thermodynamics, which has been confirmed by investigators world over²⁹⁻³³.

Experimental model for the study of irreversible thermodynamics designed by various researchers consisted of separation of two solutions by a sheet of different kinds of membranes. H. Arif^{34,35} and some physical chemists tried to examine the applicability of laws of irreversible thermodynamics to biological membrane with the help of pericardial and peritoneal of buffalo,^{36,37} toad skin³⁸, and periderm, an cuticular membrane³⁹.

Synthetic membrane history began in 1748 when French Abble Nollet demonstrated semi permeability for the first time, that animal bladder was more semi-permeable to water than to wine. One century later, Fick published his phenomenological law of diffusion, which we still use today as a first - order description of diffusion through membranes. He was also the first man to prepare and study artificial semi-permeable membranes. These membranes were made from an ether-alcohol solution of cellulose called "collodion". After that many researches were done and many inventions were found such as dialysis, different permeability of gases at rubber, osmotic pressure, and Donan's ion equilibrium phenomena.

Sartorius Werke GmbH (Germany) manufactured industrial scale membranes, microfiltration membranes, for the first time in 1950. Before that, membranes were developed in small scale for laboratory applications. However, Loeb and Sourirajan⁴⁰ discovered the very thin membrane for reverse osmosis, the asymmetri membrane which is the most fundamental breakthrough in membrane technology.

Now a days membrane applications spread over various industries: metal industries (metal recovery, pollution control, air enriching for combustion), food and biotechnology industries (separation, purification, sterilization and byproduct recovery), leather and textile industries (sensible heat recovery, pollution control and chemicals recovery). Other industries that also use membrane technology are pulp and paper industries (replacing evaporation process, pollution control, fiber and chemicals recovery), and chemical process industries (organic material separation, gas separation, recovery and recycle chemicals). Medical sector including health- pharmaceutical and medical industries (artificial organs, control release (Pharmaceutical), blood fractionation, sterilization and water purification) and waste treatment (separation of salt or other minerals and deionization).

Generally, there are several processes to synthesize membrane, some of them are sintering, stretching, track-etching, phase inversion, and coating. There are several ways to classify membranes. Based on their materials, membranes are classified as polymeric membranes, liquid membranes, solid (ceramics) membrane and ion exchange membrane. Based on their configuration, membranes are classified as flat (sheet) membrane, spiral wound, tubular, and emulsion. Based on what they do and how they perform, membranes are classified as fine filtration (micro filtration/MF, ultrafiltration/UF, nanofiltration/NF, and reverse osmosis (RO), dialysis, electrodialysis (ED), gas separation (GS), carried - mediated transport, control release, membrane electrode, and pervaporation (PV).

Membrane Processes :

Membrane processes are classified based on various driving forces, some use pressure difference (microfiltration, ultrafiltration, reverse osmosis, and piezodialysis), while others use other driving forces such as concentration difference (gas separation, pervaporation. liquid membrane and dialysis), thermal (membrane distillation, thermoosmosis) and electric (electrodialysis).

The principal advantages of membrane processes compared to other separation processes are low energy consumption, simplicity and environmental friendliness. Membrane-based separation is a result of different rate of transfer between each substance in membrane and not a result of phase equilibrium or mechanically based separation. Therefore, there is no need to add additive material such as extractor and adsorber to proceed the separation. Then we can say that membrane technology is "clean technology", in which no additive materials, which may be potential pollutants, are needed.

One of the major advantages of membrane technology is low energy consumption. Membrane based separation is not a result of phase equilibrium that takes a lot of energy to achieve and maintain. It also means that the process could be done in normal conditions where no phase change occurs. Phase change may affect the quality of materials and products. Therefore, membrane technology is suitable for the pharmaceutical, biochemical and food industries.

Designs of membrane module are very simple, compact and easy-to-use. In addition, not much auxiliary equipment is needed. There is a unique phenomenon in membrane where the scale of process and operating costs are related proportionally. This phenomenon may be caused by the modular-nature of membrane. This nature distinguishes membrane processes from other processes such as distillation, in which an increase in the process scale is followed by a decrease in cost until economical condition is reached. Not only in cost spent, but also in operating condition. Adding several modules including its auxiliary to existing system can do scaling up membrane processes.

Besides the advantages described above, membrane processes also possess several disadvantages, such as flux optimization and selectivity, material sensitivity, fouling and dependability. Until now there have been several studies conducted to overcome the disadvantages and drawbacks in membrane processes.

Flux and selectivity problems arise as an increase in flux is usually followed by a decrease in selectivity, while we aim at increasing both. Therefore membrane processes are suitable for very selective separation in which flux is not concerned such as that carried out in pharmaceutical industries.

The dependability problems arise as the characteristics of membrane differ from each other. It is due to the different characteristics of each membrane that a direct scale up of membrane processes is virtually impossible. Before a process is applied in an industrial scale, it is suggested to have a laboratory assessment of the membrane. In this way we may have better prediction on process performance.

Other major problems are material sensitivity and fouling. Polymeric membranes have limited stability (chemically, physically, and biologically), which restrict the conditions of membrane processes applied. Now a days, there are efforts to invent materials, which may overcome these constraints, Fouling causes a decline in performance of membrane processes, in which flux (performance) is very high initially but then decline drastically as materials of foulant accumulate on membrane surface. Solutions to the problem may lie in the hydrodynamic of the process and pretreatment processes.

Membrane Industry :

Membrane based market industry covers the membrane itself and its module, including additional equipment and the systems. Commercial success is one of indicator showing the important role played by membrane technology in various applications. The benefits in membrane process applications include reduced operating costs relative to competitive technology, saving of product, recovery of byproducts, savings of water, energy, chemical, etc. In effluent reduction applications, savings in transport and disposal cost become important. Membranes and membrane processes are used in four main areas, which are, in

the separation of molecular and particulate mixtures, in the controlled release of active agents, in membrane reactors and artificial organs, and in energy storage and conversion systems. Membrane has become a multi-billion-dollar business and is still growing fast. The development of membrane market is determined by energy costs, required product quality, environmental protection needs, new medical therapies, and the availability of new and better membranes and membrane processes⁴¹.

Some applications of membrane process, such as water desalination or wastewater treatment, have high industrial relevance. However, in these applications the membrane processes compete with conventional water desalination or water treatment techniques, such as multistage flash evaporation or biological sewage treatment plants. In other applications of high commercial relevance, such as in hemodialysis or in fuel cells, membranes are key components, and no economic alternative technique that could compete with membrane is currently available. There are other applications, such as the production of ultrapure water, where membrane processes compete with conventional techniques, but have a clear advantage. There are also a large number of membrane applications of lower industrial relevance, such as the dehydration of organic solvents by pervaporation or the recovery of organic vapors from waste air streams by gas and vapor permeation membranes.

Emerging Processes

Development of Improved Membranes and Membrane Materials :

Significant progress has been made during recent years in the development of new membranes and their applications. New inorganic and organic materials, super molecular structures with specific binding properties, are used as membrane materials. For the separation of gases, especially oxygen/ nitrogen and methane/

carbon dioxide, new glassy polymers and inorganic materials such as zeolites are used to produce membranes with better selectivity and higher fluxes. For the separation of enantiomers, carrier facilitated transport membranes are produced using molecular imprint techniques. In reverse osmosis, membranes with better chemical stability and higher fluxes are now available. Surface- modified membranes with better chemical stability and higher fluxes are now available. Surface- modified membranes with better compatibility and affinity membranes for the removal of endotoxins or other toxic components from blood may soon be available. The recent development in membrane technology have been assisted by new research tools, such as atomic force microscopy, acoustic time- domain reflectometry, molecular dynamic simulations, and computer-aided processes design.

High-Performance Reverse- Osmosis Membranes :

Progress that has been made in improving reverse- osmosis seawater desalination membranes during the last 20 years, which shows the salt rejection in excess of 99.5% and the water flux of various membranes by a factor of 3. The reason for this significant progress is based on the preparation technique of the barrier layer of the composite membrane, which has many folds, with the about three times larger than the area of the support structure.

Stabilization of Supported Liquid Membranes :

One of the shortcomings of today's supported liquid membranes is their short useful life. In thin membranes the solvent or carrier can be lost within several hours, which makes the membrane useless. The stability of liquid membranes can be increased drastically up to 1000 hours by placing a thin polymer layer on top of the liquid membrane.

Preparation of Composite Hollow Fiber by the Triple- Nozzle Spinneret :

Asymmetric hollow fiber or capillary membranes with a denser skin on the in or outside of the fibers are generally made by a phase inversion process. Dip-coating process is mostly used to produce composite hollow fiber membrane although it require additional production step. A triple nozzle spinneret was developed for the preparation of composite hollow-fiber membranes. The main advantage of composite hollow fibers made in one step with the triple nozzle spinneret compared to those made by dip-coating is a simplified production process because it can be done in a single production step. Generally, higher fluxes are also obtained in the single-step production, since pore penetration, which is often a problem with dip-coating, is avoided.

Inorganic Membranes for Gas and Vapor Separation With High Selectivity :

Historically, inorganic membranes are produced by a slip-coating and sintering procedure based on metal oxides such as $\alpha\text{-Al}_2\text{O}_3$. These membranes can be considered as state-of-the-art structures and are used today in micro and ultrafiltration. An interesting recent development is the preparation of zeolite membranes. Because of the unique properties of zeolite crystals such as molecular sieving, ion exchange, selective adsorption, and catalysis, these membranes have a large number of potential application in gas and vapor separation and in membrane reactors and chemical sensors. Dense inorganic membranes based on palladium and palladium alloys have been used for many years for the selective transport of hydrogen. However, their large- scale industrial applications are limited due to high price of the metal. Dense ceramic membranes based on perovskites exhibit high mixed electronic and oxygen ion conductivity, and are widely studied for applications in solid oxide fuel cells, oxygen sensors, and membrane reactors. An increasingly important research area is related to nanoporous ceramic membranes with well defined pore structures prepared by

template- assisted, self assembling methods. Furthermore, an increasing amount of research effort is concentrated on the development of proton- conducting membranes for high temperature applications in fuel cells and membrane reactors.

Development of Improved Membrane Modules :

The overall performance of the state of the art membrane modules, such as the plate and frame, the spiral wound, and the hollow fiber and capillary membrane modules has been improved gradually over recent years, and production costs have been reduced significantly. However, only very few completely new module concepts have been developed. Two exceptions are the so-called transversal flow capillary membrane module and the spiral-type tubular module. The transversal flow module is used mainly in dialysis. The characteristics of these modules are straight membrane capillaries and axial flow through the fiber lumen and the shell. In spite of the poor flow distribution, and thus mass transfer, at the shell-side membrane surface, this type of module is preferred because of its high packing density and low production costs. Spiral-type tubular membrane module involves flow around a curved tube at a sufficiently high velocity so as to produce centrifugal instabilities and secondary flow from the membrane surface to the center of the tube, and results in a substantial increase in flux. However, higher production costs and poor performance of the spiral type membrane modules have so far limited any large-scale industrial applications.

Development of Novel Membrane Processes and Applications :

New membrane processes that give a large breakthrough in its applications are demineralization by electrodeionization technique, new application in biomedical science and application in fuel cells. Actually, a significant development has been made in another process, for example, in controlling waste

gas emission by membrane contactor and membrane reactor, for both chemical as well as biological conversion. Development in membrane reactor for dehydrogenating reaction, esterification, and enzymatic reaction, seem very prospective that has been developed for a long time, however, until today its industrial application has not been seen yet. It is the same as membrane contactor for emission control. Typical study and empirical data show a large potential of this process; however, its application has also not been seen yet.

Electrodeionization and the Use of Bipolar Membranes :

Electrodeionization are used for the production of deionized water of high quality by combining conventional ion-exchange techniques with electrodialysis. The process can be operated continuously without chemical regeneration of the ion-exchange resin. The only disadvantage of the process is the relatively poor current utilization. Bipolar membranes are used today in combination with regular ion-exchange membranes for the production of acid and bases from the corresponding salts in a process referred to as electrodialytic water dissociation. A bipolar membrane consisting of a cation and an anion exchange layer arranged in parallel between two electrodes. As in electrodialysis, up to 100 cell units can be stacked between two electrodes. Electrodialytic water dissociation is a very energy efficient way. However, there are still severe problems, such as salt leakage into the products and low current utilization at high concentrations of the acid and bases.

Membrane Contactors :

In membrane contactors the membrane functions as a barrier between two phases that avoids mixing but does not control the transport rate of different components between the phases. The membrane pores are sufficiently small that capillary forces prevent direct mixing of the two phases. A key advantage of

membrane contactors is a large mass transfer area in a relatively small device. A typical large scale application of a liquid/gas contactor is the removal or delivery of dissolved gases from or to a liquid, for example, the blood oxygenation during open heart surgery, the removal of oxygen during the production of ultrapure water, and the separation of olefin/paraffin gas mixtures.

Membrane Reactors :

A membrane reactor is a device that utilizes the properties of a membrane to improve the efficiency of chemical or biochemical reaction are applied mainly in catalytic and enzymatic reactions. In the simplest form of a membrane reactor the membrane is used as a contactor that separates the catalyst from the reaction medium. The membrane merely provides a large exchange area between the catalyst and the reaction medium, but performs no separation function. It is often used in cell culture and fermentation processes such as the enzymatic degradation of pectin in fruit juice. In the second type of membrane reactor the membrane shows the selective mass transport properties, and is used to shift the equilibrium of a chemical reaction by selectivity removing the reaction products, for example, in dehydrogenation or oxygenation reactions such as the dehydrogenation of n-butane. The third type of membrane reactor combines the membrane contactor and separation function, such as in enzyme catalyzed deesterification reactions.

Membrane for Fuel Cells/ Electrolysis :

One breakthrough in the application of ionic conducting polymer membranes is the proton exchange membrane fuel cell, a device that converts chemical energy directly into electrical energy without burning. As the electrochemical combination of hydrogen (the fuel) and oxygen produce water, the fuel cell is environmentally clean and is expected to replace the gasoline engine or rechargeable battery in the automobiles.

Synthetic Membranes in Medical Applications :

Biomedical applications are by far the most relevant used in medical devices such as hemodialysers, blood oxygenators, and controlled drug-delivery systems. There is, however, a substantial effort focused on the development of the membrane for the next generation of artificial organs, such as the artificial liver or artificial pancreas. In this device, as in other novel vehicles for the delivery of cell and gene therapy, synthetic membranes are combined with living cells to form so-called biohybrid organs.

Breakthrough in Industrial Application :

Membrane processes cover a wide range of application from (waste) water treatment to medical application. For some application, membranes play an important role in which other technologies are not capable such as in medical sector (hemodialysis) and energy sector (fuel cell).

Membrane technology also makes a breakthrough in water treatment. A revolutionary water treatment process was accomplished by corporate membrane into the treatment process resulting in high effluent quality. Water treatment has become an important issue regarding the scarcity of clean water sources. A huge supply of water that covers the earth in the form of ocean can not fulfill the needs of water readily considering conventional desalination process that must be done before it can be used as potable water. Desalination with distillation process popular in 1970s is not attractive anymore because of its high capital cost and wide space demand. In area with high minerals content, distillation process are also susceptible to corrosion.

Conventional water treatments are not capable in producing potable water that fulfill the requirement of water quality standard that becoming more stringent now a days. An advanced water treatment like ozonation and activated carbon can improve water quality but on other hand add in a difficulty in operation and cost.

Membrane technology offers one or two simple steps to overcome it. Membrane as highly selective layer is capable to separate micro organisms and pathogens completely. Membranes are also capable of reducing hardness, controlling color, and removing inorganic and organic compounds. Four membrane processes have direct application for potable water treatments are RO, NF, UF, and MF. These pressure driven processes differ in the size of the membrane pores, types of constituents removed, and the way removal is achieved⁴⁴. Water with low quality is acceptable to be processed by membrane. In space demand, membrane processes require a smaller, space compared with conventional technology.

Technology for waste water treatment that might provide several advantages compared with conventional biological process alone is membrane bioreactor. Membrane bioreactor (MBR) can be defined as the combination of two basic processes, biological degradation and membrane separation. Biological process commonly used for wastewater treatment combined with membrane process is activated sludge process. Currently, the majority of installed MBR system are being used for the treatment of wastewater from the automotive, cosmetic, metal fabrication, food and beverage processing, landfill leachate, and other industries⁴⁵. MBR can be categorized into three types that are MBR for biomass separation, MBR for aeration, and MBR for pollutants extraction. Submerged membrane bioreactor for biomass separation is a breakthrough in membrane bioreactor field for industrial wastewater treatment. The submerged MBR system should be distinguished from other MBR system, in this system membrane is installed inside biological reactor.

EDI (electrodeionization) is a continuous chemical-free deionization process that relies on the same fundamental principle as for mixed-bed ion exchange. An EDI stack consists of diluted compartments, concentrated compartments and electrode compartments. The diluted compartments are filled

with mixed-bed ion exchange resins, which enhance the transport toward the ion exchange membranes under the force of a direct current. The later configuration, both diluted compartments and concentrated compartments are filled with mixed-bed ion exchange resins. Since the concentration of ions is reduced in the diluted compartment and is increased in the concentrated compartment, the process can be used for either purification or concentration.

An extended investigation of operating conditions and performance of the EDI process has been conducted by Matejka⁴⁴ for high purity water production from brackish or tap water. The initial commercialization of EDI systems have been applied worldwide to meet the need of high purity water, such as in pharmaceuticals, semiconductors, power, and high quality optics industries. Limited ability of existing technology to reduce especially the need of high water production cost effectively and environment friendly offers a significant market opportunity for the commercialization of EDI systems.

Outline of the Present Work :

The systems under investigation are (i) Newly developed Parchment supported lead tungstate model membrane and (ii) Hen egg (*Gallus saneratii*) shell biological membrane. The thesis has been described under the following aspects of "Membrane Phenomena".

- (1) Evaluation of thermodynamically effective fixed charge density by the use of the following:
 - (a) Classical method of Teorell - Meyer - Sievers (TMS)^{43, 40}
 - (b) Altug and Hair⁴⁷ Method, which is the modification of TMS method.
 - (c) Kobatake et al.^{26, 27}, Nagasawa et al.²⁸ and Aizawa et al.⁴⁸ methods based on the thermodynamics of irreversible processes.
- (2) Test of the theories of membrane potential and bi-ionic potential given by Toyoshima et al.⁴⁹ based on thermodynamics of irreversible process.

- (3) The difference theories of impedance characteristics by Warburg⁵⁰, McDonald⁵¹ and Armstrong and Archur⁵² have been used for analyzing different model - equivalent electrical circuits.

Parchment is greatly refined from leather. The skins of various animals cattle, sheep and goats being most common-are washed and divested by hair or wool. Then the skin is stretched tight on a frame, scraped thin to remove further traces of hair and flesh, whitened with chalk and smoothed with pumice. Tradition narrates that it was invented as the result of book - collecting rivalry between Ptolemy V of Egypt and Eumenes II of Pergamum about 190 B.C. Fearing the library at Pergamum might outstrip the collections at Alexandria, Ptolemy placed an embargo on papyrus to prevent his rival from making any more books, where upon Eumenes made parchment. In some support of the tradition stands the fact that both Greek and Latin words for parchment mean "Stuff from Pergamum".

The choice of taking parchment membrane is entirely on the suggestion of Prof. T. Teorell⁵³, delivering Eight Spiers Memorial Lecturer on "Transport Phenomena in Membranes". He has emphasized on the need of studying parchment membrane in the following words.

"My own interest and the starting point of my work on membrane and their behaviour was a very definite one. I think it was rather typical of many biologists or medical research people like myself. As a research student I wanted to work on the problem of stomach ulcer formation and did some experiments on the cat's stomach, on how its hydrochloric acid was produced and how its acidity was "regulated". Soon it was possible to demonstrate that the gastric mucosal membrane, in some formal aspects at least, behaved exactly like a parchment membrane. It could exchange ions by dialysis across it that way it was possible for us to propose a hypothesis for so-called "Acidity regulation" of the stomach, which has since been tested in various medical quarters. The finding that

electrolyte transport processes in the stomach could be handled by something similar to Fick's diffusion law and that Nernst - Planck's formulae for electrical potential were applicable, encouraged me to proceed further".

The contents of the thesis has been artificially separated and presented under the following heads for clarity, although certain amount of overlap has occurred. This type of overlap is permitted as it helps in the elucidation of the topic under discussion.

Chapter -I. Introduction :

This Chapter is the general introduction describing the background literature relevant to the present work and the history of membrane science and technology, viz. its origin, development and further fragmentation into a highly sophisticated discipline which makes its presence felt in almost every modern and cutting-edge technology, directly affecting the welfare of mankind .

Chapter -II. Objective of the Work :

This chapter describes the general purpose of the present work, development, chemical characterization and applications that would be feasible for electrochemical studies.

Chapter - III. Structural Studies of the Model and Biological Membranes :

This chapter depicts the basic properties of model and biological membranes and existing artificial and biomembrane models. This portion also gives an idea about the general structure of the model and biological membranes with the help of Scanning electron microscopy (SEM), Transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FTIR). The SEM gives the superficial structure of the membrane while TEM reveals its internal mysteries. FTIR further dissects the internal structure of the membrane which unrables the composition of the membrane.

Chapter-IV. Electrochemical Theories Based on Non Equilibrium Thermodynamics.

This chapter is related with the basic theories of membrane phenomena based on the principles of non equilibrium thermodynamics. Electrochemical studies of biological and model membranes are totally based on certain widely accepted theories of irreversible thermodynamics. Various theoretical equation have already been derived by many workers in order to evaluate important parameters governing the membrane phenomena regarding their electrochemical characterisation. Basically various approaches are taken into account by the author for the establishment of recent theories for membrane potential, Bi-ionic potential charge density membrane and impedance etc. Which are the base on the behalf experimental measurements for the characterisation of the membranes.

Chapter-V. Transport Studies Based on Membrane Potential Measurements:

This chapter deals with the measurements of membrane potential across the parchment supported lead tungstate model membrane and hen egg (*Gallus saneratii*) shell biological membrane using various 1:1 electrolytes of different concentration under isothermal conditions for the evaluation of thermodynamically effective fixed charge density of the membranes as well as to examine the validity of the recently developed theories for membrane potential based on the thermodynamics of irreversible processes.

Chapter -VI. Studies of Membrane Selectivity for Metal Ions :

This chapter is devoted to the evaluation of membrane selectivity of parchment supported lead tungstate model membrane and hen egg (*Gallus saneratii*) shell biological membrane towards the metal ions from membrane potential and bi-ionic potential measurements for various 1:1 electrolyte system, The experimentally observed values of membrane conductance for the same

electrolyte system are also actively involved to establish the selectively order of metal ions in the membrane phase.

Chapter-VII. Membrane Characterization Using Impedance Measurements:

This chapter concern about the electrical resistance, and capacitance of the parchment supported lead tungstate model membrane and the hen egg (*Gallus saneratii*) shell biological membrane have measured experimentally using 1:1 electrolyte in order to establish impedance characterization of the membranes.

Chapter- VIII. Future Prospects :

This Chapter highlights the uses of membrane science and technology in various discipline and industries namely, food and biotechnology industries, leather and textile industry, dairy industry, medical sector, reverse osmosis, bioreactors, biomedical devices, and various others.

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Chapter- II

Objective of the Work

The general purpose of the work presented in the thesis is the development, chemical characterization and application of the parchment supported lead tungstate model and hen egg (*Gallus saneratii*) shell biological membranes that would be feasible for electrochemical studies. On the basis of the background literature presented in the Introduction of the thesis. The following specific objectives were set :

(i) Development :

The aim is to develop a stable and reproducible model membrane that is free from substrate-induced defects. Control of membrane composition and state was desirable. In addition, the model system was to allow for studies of transmembrane ion transfer.

(ii) Characterisation :

The model membrane is to be characterized by a variety of electrochemical methods to assess its consistency to a biological membrane. Theoretical modeling was to be carried out in parallel to the experimental characterization, to support and explain experimental observations. In addition, if implementable, optical and spectroscopic techniques would be employed in the characterization.

(iii) Applications :

The applicability of the development model system may be in the probing of ion transfer, ion – membrane interactions and membrane

activity of biotechnological drugs, ion sensor techniques, fuel cell technology, biomedical devices, bioreactors, electrochemical systems are some applications of interest. In fact today there is almost no discipline of science which does not bear the impact of membrane technology. Be it biomedical sciences, biochemical sciences, biotechnology or biochemistry.

(iv) Future prospects :

Membrane science will play a very significant and vital role in the hygienic and healthy living of human being in the days to come. In the simplest form membrane technology will be useful in the provision of adequate quality of water for urban environment and the treatment of waste water to protect the environment, whereas it will also be helpful in medical field in its complex form where it will be solving various medical difficulties in the treatment of different diseases for example synthetic membranes will help in organ transplantation. By enclosing the concerned organ and thereby protecting it from rejection. In future artificial or natural membranes may be synthesized which could form liposomes which are stable in the human body and act as drug delivery agent for instance drugs enclosed by liposomes which mimic the plasma membrane of the cell may be synthesized and injected into the patient. This approach helps in the slow release of substances or drugs and increases the bioavailability of the drug for its effective action.

Chapter - III

Structural Studies of the Model and Biological Membranes

Introduction

The transport of matter through membranes is a basic phenomena of life. All organisms are separated from their environment by special membrane barriers which control the exchange of matter with their surroundings. In addition, nearly all life processes are intimately involved with membranes processes. Thus membrane play a central role in the transformation of metabolic energy into osmotic, electrical and to some extent mechanical work, in the acquisition and processing of information, and also, though to a lesser extent, in reproduction. In view of this multiplicity of functions, it is not surprising that the term biological membrane has no simple definition.

Membrane technology is a highly fragmented technology, covering such wide ranging applications as reverse osmosis, desalination, ion sensor techniques, fuel cell technology, electrical storage batteries, nanotechnology, controlled release pharmaceutical formulation, separation in pharmaceuticals and fermentation process, separation technology in fruit and vegetable processing, pre-concentration of milk before cheese, air pollution, petroleum engineering, biomedical devices, bio-reactors, electrochemical systems and several others processes. The scientific and engineering disciplines involved are also varied, and includes physical and polymer chemistry, electrochemistry and chemical engineering. But the glue that binds all of these varied applications and discipline together is transport across membranes.

The recent progress pertaining to membrane diffusion and transport problems has been achieved in varying fields like chemistry, bio-chemistry, physiology, pharmacology, biophysics, industrial chemistry, chemical

engineering, etc. in which the starting points and aims have been different. Physicochemical attacks have been made on several biological problems, which are well described, but badly explained. Surface chemistry, solution theory, colloid chemistry, electro chemistry etc. have been employed to solve biological problems. There are several areas of membrane research which have potentially far-reaching consequences to medicine and chemical industry. Work in this field is contributing significantly to the economic prosperity and physical well being of all mankind.

From the point of view of a physical chemist the knowledge of transport processes across artificial membranes if applied in the right direction can solve many secrets of nature. The biologists have recently employed more quantitative methods of research and accumulated enormous data suitable for theoretical studies. Membranes of varying degree of permeability and semi permeability occur universally in plants, animals and organisms, constituting the fundamental devices which regulate the exchange of material and thus the flux of life.

Electrochemistry is pertinent in membrane studies according to Buck¹ at three levels. One is the development of techniques with applications to experimental phenomenology including current-voltage-time- concentration behavior and second is the mathematical modelling implied by experiment and tested against experiment. The third level is experimental verification of models in terms of the molecular processes and properties and includes determination of theoretical parameters by electrical methods and by complementary non electrochemical methods, physical, optical, ESR, FTIR, XRD, SEM, TEM, DSC, SWAXS, DLS, LB, IS and Zetasizer etc. From transient and steady state measurement of current or membrane potential as a function of chemical composition, chemical treatment, and temperature, the roles of kinetic and equilibrium parameters can be deduced or inferred. A possible approach to modelling begins with the assumption of the membrane as a linear system to

which laws of network theory may be applied. Another begins by solution of basic electrodiffusion laws of transport with equilibrium or kinetic boundary conditions in order to deduce forms for system functions which satisfy the data.

The impact of membrane technology on analytical chemistry according to Buck¹ is twofold: the development of membrane systems responding in predictable ways to ionic solution activities has already provided a new dimension in electroanalytical chemistry. This is the technology of ion selective electrodes and membrane sensors. However, the second and possibly the major aspect of analytical chemistry affected by membrane technology is analytical separation science. In a particularly lucid table by Lakshminarayanaiah², all presently known membrane phenomena are placed into categories according to the driving forces acting within or across membranes : gradients of chemical potential, electrochemical potentials, pressure, temperature and combinations of these. There are many items which may be considered as techniques, of analytical separations. Among these are techniques whose development and application belong mainly in the domains of clinical and medical chemistry, physiology, pathology, chemical engineering, industrial chemistry, nanotechnology, and the various ecological and public health sciences. They are none the less capable of practical application and extension in the analytical laboratory.

The literature in the form of papers and in book form describing membrane technology and applications is far too extensive to mention. However, the work of Hills and his students³⁻¹⁴ is of fundamental nature. The principal recent volumes containing significant sections on, or totally devoted to membrane electrochemistry are by Helfferich¹⁵, Cole¹⁶, Lakshminarayanaiah^{2,17-22}, Hope²³, Roper²⁴, Plonsey²⁵, and Janacek²⁶. Continuing series are edited by Bittar²⁷, Eisenman²⁸, and Cadenhead et al.²⁹.

Applications of membrane electrochemistry to yield activity sensing electrodes are amply described in books edited by Eisenman³⁰ and Durst³¹. Sensor techniques are now sufficiently advanced to discuss recently at several national and international conferences. This field has also been the subject of numerous general reviews³²⁻⁴⁰ and as many specialized reviews. Recently published papers of ion selective electrodes⁴¹⁻⁴⁶ reports the applications of membrane as membrane electrodes in various forms. However, this field has produced such a variety of new measuring devices and had opened so many analytical possibilities in terms of new analysis and new detection system. The renounced explanations in the field of membrane science were shown in the review "The growth of Membrane Technology" of H.K. Lonsdale⁴⁷ includes the various membranes fabricated by the scientists using the different techniques. Numerous recent volumes are concerned, in part, with membrane electrochemistry⁴⁸⁻⁵⁴.

Model Membranes

Model membrane may be described¹⁷ as "A phase, usually heterogeneous, acting as a barrier to the flow of molecular and ionic species present in the liquid and/or vapours contacting the two surfaces." The term heterogeneous has been used to indicate the internal physical structure and external physicochemical performance⁵⁵⁻⁵⁸. From this point of view, most membranes in general, are to be considered, heterogeneous, despite the fact that conventionally membrane prepared from coherent gels have been called homogeneous. Inorganic membranes are of great importance for many applications of practical interest because of their ability to withstand impairment even when used in aggressive environment and at high temperature.

The terms homogeneous versus heterogeneous proves to be an important distinction from the point of view of mass transport. In the dilute solution limit, the friction coefficients for mass transport by diffusion or migration are interconvertible by Onsager reciprocal relation, and both can be related to jump

distances and frequencies according to random walk models, as long as there are no preferred regions of low friction in the membrane, it is isotopic on a molecular level and is considered to be homogeneous. Uniformity of mesh on a molecular scale is another view of homogeneity, channel free solid and liquid membranes are usually homogeneous and two phase membranes, such as solid crystallites imbedded in a nonionic resin are clearly heterogeneous. The distinction, however, is not always essential⁵⁹.

Structure and Composition :

Membranes may be solid, liquid, or gas⁶⁰ and the outer phases are usually liquid or solid. Although it is frequently the case that membranes are thin in one dimension relative to the other two dimensions. This property is only functional or operational. In order to achieve a measurable chemical or electrochemical effect and to make chemical or electrochemical measurements on a membrane system in a reasonable time, some transport related, property must be susceptible to temporal change. Thus, a change in potential, flux, or concentration (among many varying measurable quantities) require sample thicknesses such that $d^2/2D$ is comparable with the observation time (D is a mean diffusion coefficient). Although irregularly shaped membranes are conceivable, most theories and experiments are restricted to systems with one dimensional or spherical symmetry such that transport occurs in one dimension, the X direction in parallel face planer membrane or along a radius in membrane with spherical shape.

Membrane are considered to be porous or non-porous depending upon the extent of solvent penetration¹⁸. At the non-porous extreme are membranes which are non-ionic and contain negligible transportable species at equilibrium. Ceramics, quartz, anthracene crystal and teflon films between metal electrodes or electrolyte bathing solutions are solid membrane examples. Organic liquid films such as hydrocarbons and fluorocarbons in contact with aqueous electrolytes are liquid membranes, which can be solvated and will contain components from the outer

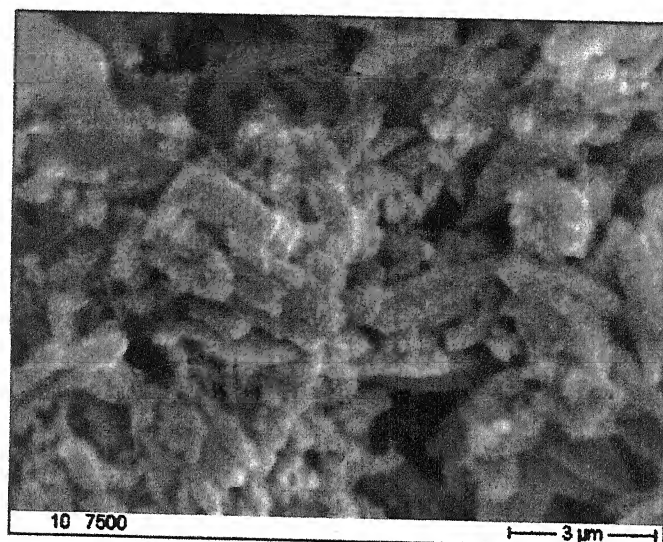
phases. Among these are non-ionic films such as cellophane, inorganic gels and loosely compressed powders in contact with aqueous solutions. These materials absorb solvent from the surrounding media and may also extract other neutral molecules and ionic salts. More widely studied are these membranes of polyelectrolytes ("solid" ion exchangers) aqueous immiscible organic liquid electrolytes ("liquid" ion exchangers)^{15,18,19}, various parchment supported inorganic precipitates⁶¹⁻⁷², solid ion conducting electrolytes, including silver halides, rare earth fluorides alkali silicate and alumino-silicate glasses^{30,31,73,74}. All of these materials contain ionic or ionizable groups within the membrane which are capable of transport under diffusive or electric field forces. In addition, these materials possess the properties of porosity, polyelectrolytes tend to swell rapidly by osmotic pressure driven uptake of solvent. Liquid ion exchangers are surprisingly slow to take up water, while the inorganic salts have no tendency to hydrate. Glass membranes are complicated by simultaneous hydrolysis of the polyelectrolyte during uptake of water⁷⁵⁻⁷⁷.

The frequent use of charged and uncharged in the membrane literature is usually unsound electrostatically, but does provide an intuitive chemical description. For example, charged membrane usually refer to electrolyte membrane such as solid and liquid ion exchangers where the fixed and mobile sites are the charges. Actually these membranes are quasi-electroneutral in their bulk when the thickness is large compared with the Debye thickness at each interface. Quasi-electroneutrality means that in any volume element large compared with the distance between ions, the sum of ionic charge $\sum_i \bar{z}_i \bar{c}_i = 0$. In the literature, uncharged membranes are those, like cellophane, with no fixed charges. This frequently used literature definition provides no place for liquid bilayer membranes which are electrostatically neutral only in the absence of charge carriers and in the absence of bathing solutions whose salts possess preferential solubility of anion over cation or vice-versa, but are usually electrostatically charged by an amount of ions of one

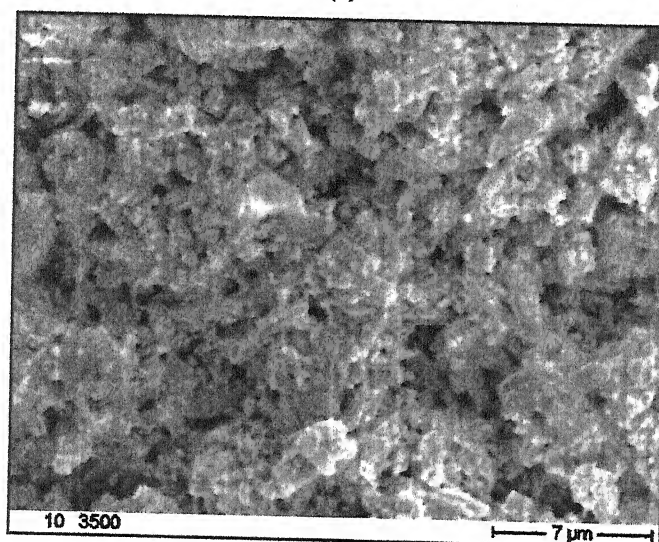
sign in normal operation. Thick hydrocarbon membranes and membranes of diphenyl ether (or derivatives), phthalate, and sebacate esters are generally neutral in the presence of most bathing electrolytes, but may be charged electrostatically, depending on thickness, in the presence of neutral carrier species which preferentially solubilize ions of one sign. The use of the terms charged and uncharged to describe electrolyte or non-electrolyte membrane has been discouraged unless the precise electrostatic connotation is involved⁵⁹.

SEM investigation of lead tungstate membrane morphology :

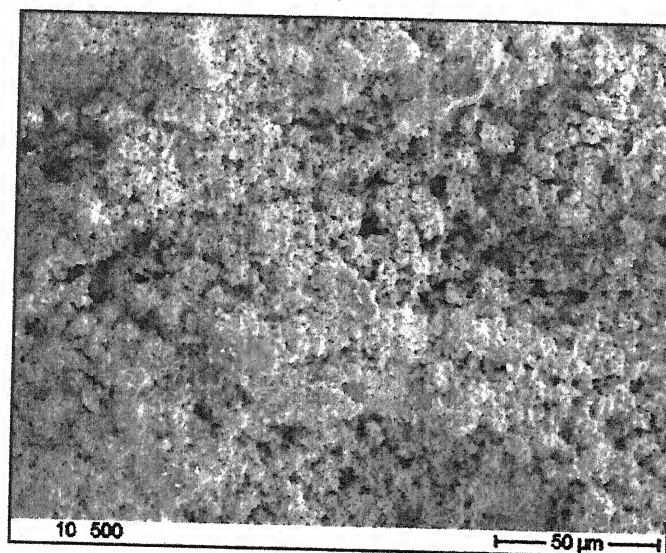
Inorganic precipitate membranes because of their stability in various environmental situations have quite often been utilized as a model for the studies of transport phenomena. I have in a series⁶⁸⁻⁷² of papers, reported the preparation of various types of membranes using inorganic precipitates and have utilized them as a model to study the mechanism of transport of ions. Recently, a number of investigators while developing precipitates/ membranes have frequently utilized scanning electron microscope (SEM) images for their characterization. The composite pore structure, micro/ macro porosity, homogeneity, thickness cracks and surface texture/ morphology have been specially studied by scanning electron microscopy. The information obtained from microscopic images has provided guidance in the preparation of well ordered precipitates and/or crack-free membranes. Consequently, the scanning electron microscopy (SEM) model Phillips 515, USA, investigation was carried out for structural characterization and elucidation for newly developed parchment supported lead tungstate membrane. The SEM surface images of the lead tungstate membrane were taken and are presented in Figs. (3.1, a-c). SEM images appear to be composed of dense aggregation of smaller particles and formed pores probably with non-linear channels with fully interconnected. Particles are irregularly condensed and adopt a heterogeneous structure comprising masses of various size.



(a)



(b)



(c)

Fig. 3.1 (a-c)
Scanning electron micrographs (SEM) of parchment supported lead tungstate model membrane

FTIR studies of lead tungstate membrane :

The Fourier transform infrared spectroscopic studies on membrane has also been carried out first time to explore the exact structure of parchment supported lead tungstate model membrane so that its practical use in the field of food and biotechnology industry, leather and textile industry, medical sector including health- pharmaceutical and waste treatment etc. may be ascertained on the basis of its structure.

Lead tungstate model membrane has been prepared in the laboratory by the method of interaction as suggested by Beg and coworkers⁶¹⁻⁶³, the detail is given in the experimental part of the chapter V. To carry out FTIR measurements, sample membrane was ground in powder form and them mixed with dehydrated KBr powder. Both were then mixed with properly to form pellets using 10 tonn hydraulic press. The partly transparent pellets were used to record FTIR spectra in transmission mode.

The FTIR spectra were recorded on Perkin- Eimer instrument model spectrum BX series, (USA) in the region $200-4400\text{ cm}^{-1}$. The FTIR spectra for lead tungstate membrane has been displayed in Fig. (3.2) by the blue spectra. The sample spectra has also been compared with Fluka library to find out possible structure of same membrane as displayed in Fig. (3.2) by red spectra.

On comparision it has been found that it shows the similarities with following compounds with percentage probability given in Table 3.1. Peak table with % transmission has also been given in Table 3.2.

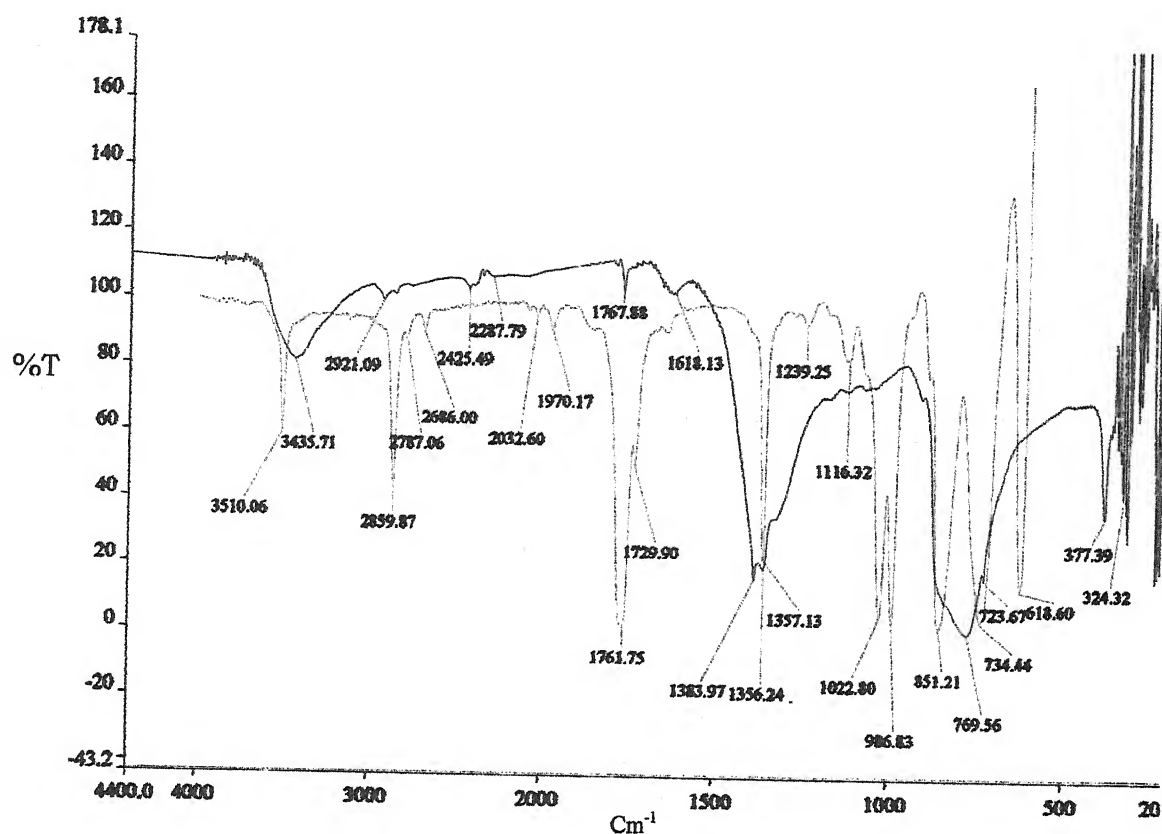


Fig. 3.2

FTIR Spectra of parchment supported lead tungstate model membrane.

Table 3.1

Percentage structural probability of the lead tungstate model membrane

% Probability	Compound
0.932	Chloral anhydrous
0.929	Methylamine anhydrous
0.928	Carbon tetrachloride
0.911	1,2- Di iodoethane
0.889	Hexachloro-2-propanone
0.871	Trichloro acetonitrile
0.855	Epichlorohydrin
0.844	Chlorocarbonyl sulfonyl chloride

Table 3.2

Peak table with % transmission of lead tungstate model membrane.

Peak No.	Wave number (cm^{-1})	% Transmission
1	3435.71	81.48
2	2921.09	99.93
3	1767.88	103.48
4	1618.13	102.94
5	1383.97	17.16
6	1356.24	20.36
7	769.56	1.27
8	377.39	36.67

The above studies shows that the parchment supported lead tungstate model membrane has the presence of IR active bands. This study will be helpful to assign the exact structure of the lead tungstate membrane and then in turn to have its applications in the various field of practical interest.

Classification :

Membrane may be broadly classified into natural and artificial. Natural membranes are considered to posses a fundamental unit membrane structure which is a bimolecular leaflet of lipid with polar groups oriented towards the two aqueous phases of the cell, and protein is supposed to exist close to the polar heads of the leaflet. This type of universal structure is absent in artificial membranes.

Lakshminarayanaiah¹⁸ has given a classification of membranes on the basis of the preparation under the heads : (A) Operationally useful membranes (i) Homogeneous, and (ii) Heterogeneous membranes which are subdivided into (a) non-reinforced membrane, (b) fabric backed or reinforced membranes, (c) membranes formed by chemical treatment of other films or membranes, (d)

membranes formed by the mechanical treatment of the membrane forming monomers or polymers, and (e) membranes formed by photochemical treatment, (B) Membranes to serve as models for natural membranes (C) Composite and other special membranes.

Membranes can also be categorized according to whether it contains sites for ion exchange or it is site-free, and it is an ion exchanger, according to whether its sites are fixed or mobile and whether the sites and their counter ions are associated or dissociated, the mechanism of ion transport across a membrane with mobile carrier is given in (Fig. 3.3). This type of classification has been presented by Eisenman, Sandblom and Walker⁷⁸. These authors have, however, restricted their discussion to membranes whose properties are considered to be homogeneous in the plane of the membrane, and have avoided explicitly with the complexities which results from either mozaic membranes, in which local eddy current occur⁷⁹ or series membranes, in which space-charge regions exist analogous to those at p-n semiconductor junction⁸⁰.

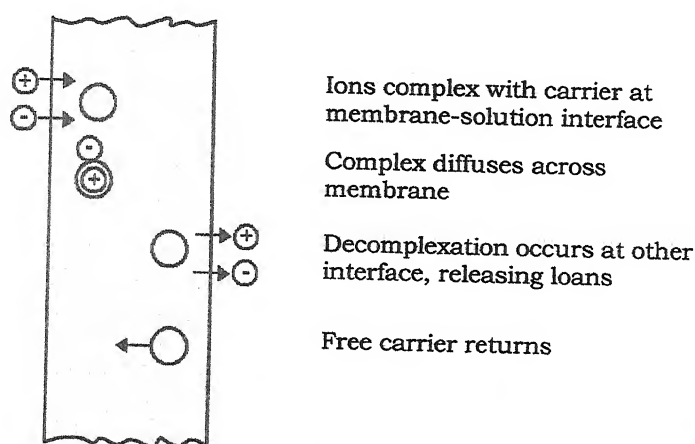


Fig. 3.3

The mechanism of ion transport across a membrane with a mobile carrier.

Unlike the classification based on membrane structure, membrane are usually classified either on the basis of their nature, i.e., coherent gel or otherwise, or on the nature of chemical reaction involved in their formation, i.e., addition or

condensation reaction. The efforts of various workers have been directed towards (A) Preparing membranes of good chemical and mechanical stability and favourable electrical performances suitable for fundamental transport studies and for applications in some industrial operations such as the treatment of brackish water, saline water conversion, etc. (B) Building suitable models to mimic the properties of natural membranes, and (C) Preparing composite membranes containing cationic and anionic groups in suitable arrangement to demonstrate and to study the physicochemical phenomena associated with rectification of alternating current and other special membrane for specific purposes as given in Fig. (3.4).

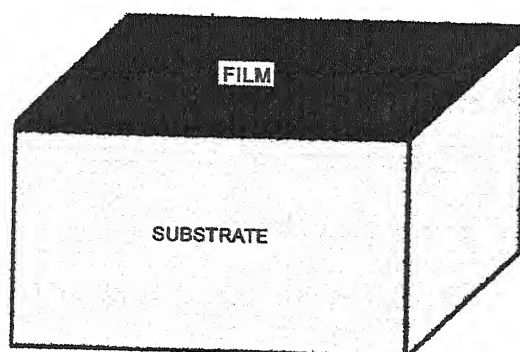


Fig. 3.4

Model composite membrane

It is worthwhile to mention that most of the work concerning category (A) seems to be directed towards finding suitable membrane materials for fabricating a structure for effective desalting of sea water by application of pressure. The most commonly used material for casting a membrane for desalination is cellulose acetate, although, polymethacrylic acid (PMA), phenolsulphonic acid (PSA), polystyrene sulphonic acid (PSSA) and cellulose esters have proved very useful¹⁸⁻²⁰. In category (B) bilayer membranes, first generated by Mueller⁸¹, have most widely been used a model for living cells and the studies have given

somewhat a better understanding of the structure and function of natural membranes. The membranes of category (C) are quite numerous^{20,59,82-84}.

The common ion-exchange membranes having an organic matrix are largely employed in several technological processes. The first inorganic ion exchange membrane, possessing very high resistance towards acid, temperature and ionizing radiations and having, at the same time, a high concentration of fixed charges, were obtained two decades ago, independently by Bregman⁸⁵ and Alberti⁸⁶ who used amorphous zirconium phosphate as an active inorganic material. Inorganic ion-exchange membranes have acquired particular significance in these two decades. These membranes have several advantages over organic ion-exchangers, e.g., their ability to withstand ionising radiations and very high temperatures without undergoing degradation and their remarkably high selectivity⁸⁷. Due to the ability of membranes to remain stable at relatively high temperatures, to resist degradation and fouling and to remain stable under corrosive and oxidising conditions, they have great utility in electrical membrane separatory processes; particularly in electrodialysis and transport depletion process. Their high electrical conductivity and better current efficiency have found their use in cells for the electrolytic desalting of brackish water^{88,89,90}, fuel cells and electrical storage batteries⁹¹ where extremely strong, ion selective, membranes are required to maintain ion separation between the electrodes of the battery or fuel cell and wherein operating temperatures may approach and exceed 125°C. The inorganic ion-exchange membranes are useful in a variety of selective separation process, such as water purification, and to process other solvents having soluble ionic contaminants. However, they have made little headway as models for biological membranes inspite of the fact that comparatively simpler inorganic systems made up of amino, imido and phosphate groups comparable, it say, phospholipids can be envisaged and subsequently synthesised.

Two types of inorganic ion-exchangers are generally known, viz., (i) crystalline and (ii) amorphons, heteropolysalts such as phosphomolybdates, alumino silicates^{92,93} etc. belong to the former category, and the simple and mixed of group IV, V and VI to the latter category⁹⁴. They also differ in their permeability. In order to obtain them as sheets of sufficient mechanical strength they are amalgamated with polystyrene⁹⁵⁻⁹⁸ and for the purpose of basic studies, parchment supported membranes are mostly employed⁶¹⁻⁷².

According to Lonsdale,⁴⁷ "membranes of traditional type are very inefficient separation devices and for two very good reasons- first they are too slow and second, they are too non-selective." They are too slow for most conventional separations because the diffusion coefficients of most permeants of interest in polymeric membranes are quite low of the order of 10^{-7} cm²/ sec for the permanent gases; two or three orders of magnitude lower for permeants of molecular weight 100 to 300, and virtually unmeasurable for permeants with molecular weight 1000.

Secondly they are generally insufficiently selective, for it is required that frequently all of type A molecules to pass and none of type B or any other type. In most cases, membrane separators are no match in this regard for the multi-effect distillation column. Even silicone rubber membranes in spite of their very high permeability, have made limited headway in the separations field because of their very low permselectivity. (Actually ultrathin silicone rubber membranes are now finding application in the enrichment of O₂ in air).

Loeb and Sourirajan⁹⁹ developed the exquisitely thin skinned cellulose acetate membrane for water desalination by reverse osmosis. Since then, others have found alternate ways of making membranes that are effectively exceedingly thin. Some of these go down to a few hundred Angstrom units in thickness, without apparent imperfections, thereby nearly rivaling the 80 Å⁰

cell membrane in thickness. The synthetic membranes require support for strength but, based on both electron microscopic examination and flux measurements on both conventional thick films and interfacially polymerized thin film Fig. (3.5) and ultra thin films of the same material, the effective thickness of these new membranes is as stated. This, then, was one solution to the problem of low flux. And it led to the reverse osmosis industry.

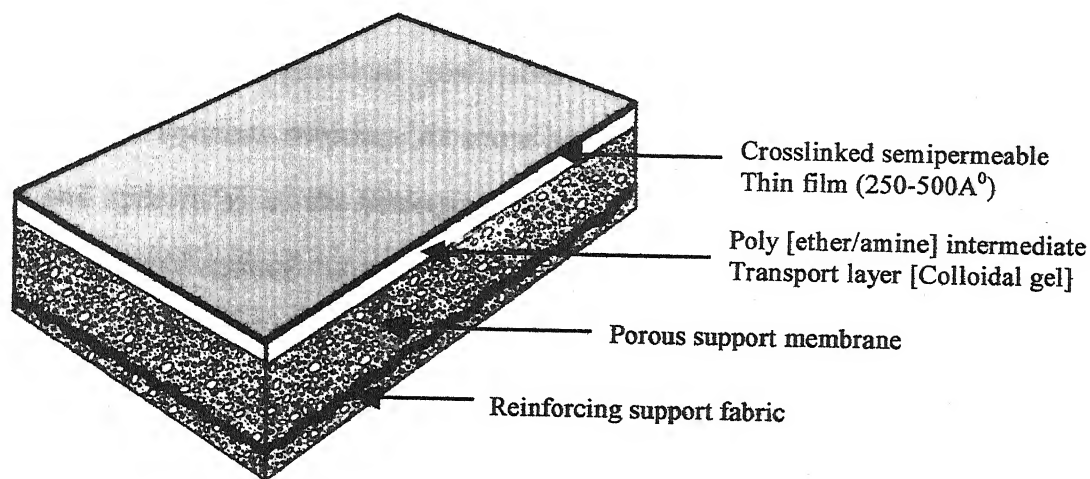


Fig. 3.5

An interfacially polymerized, thin-film composite membrane in cross section.

A second solution to the problem of slowness is even newer, so new, in fact, that it has not yet reached commercial realization, although it appears destined to do so. That approach is based on the use of liquid membranes, in which diffusion coefficients are typically 10^{-5} to 10^{-6} cm^2/sec instead of 10^{-7} to 10^{-10} cm^2/sec as in polymeric films. But the real breakthrough associated with liquid membranes is not the high fluxes they permit, but the high selectivities, for the liquid membranes under development today all contain carriers of some sort. With carriers the membranes become extremely permselective, in some cases transporting a favoured species to the exclusion of unfavoured species with separation factors of a thousand or more. Still more interesting, these new membranes readily permit "uphill" diffusion, so that desired species cannot

only be cleanly separated from undesired species but concentrated many-fold-actually, many thousand-fold - at the same time. The transport process is variously known as coupled or facilitated transport, and it is reminiscent of the process known as active transport in the biological membranes.

For these reasons, then, there is a quiet revolution occurring in membrane separation technology. In the near term, we can reasonably expect increasing application of membranes to gas separations, Beyond that, one can readily envision the practical realization of quite clean, highly specific separations in aqueous solution. At some point, membranes may rival both the speed and specificity of the biological membrane, and the uses to which they may be put could exceed our present ability to project.

Biological Membranes

Transport studies across biological membranes are quite difficult due to their thin delicate structure, difficulties in isolation and complex surface characteristics¹⁰⁰⁻¹⁰¹. Several attempts have been made to explain the phenomena of living systems by making experimental observation across an analogous membranes which has similar surface and lipid-protein structure as encountered in the case of biomembranes. As *in vivo* studies are extremely difficult, most of the transport studies are made *in vitro* condition i.e. by isolating membrane from living organism. Several studies reporting different characteristics like transport of water and salt permeation, diffusion of weak acids, reflection coefficient of number of non electrolytes, pharmacological and biochemical interaction, feed back inhibition of sodium uptake etc. of bladders of rabbit, sheep, toad, goldfish, rat, goat etc. and pericardial and peritoneal of buffalo, Periderm, an cuticular membranes etc. are available in literature¹⁰²⁻¹¹⁶. Earlier studies on transport processes, in both artificial and natural membranes have revealed some useful information. From these studies on permeability of

membranes, it can be assessed¹¹⁷ (i) whether the movement occurs through the bulk of the membrane or through specific limited region of membrane, (ii) whether it is brought about by the action of the specific membrane component which is used in explaining structural relationship of the membrane with permeating species.

The description of transport phenomena in biological membranes is still unclear from the view point of physical chemistry, Transport phenomena in ion exchange membranes can be controlled by several factors such ionic concentration within the membrane, fixed charge concentration, solution composition, ionic fluxes, and water content. The ionic transport as well as distinctive selectivity is provided by fixed groups in the ion exchange membrane, but that of co-ions is strongly restricted due to Donnan effect. The fixed charge theory was first proposed by Teorell¹¹⁸⁻¹¹⁹, Meyer and Sievers¹²⁰⁻¹²¹, who describe the Donnan equilibria at the membrane-solution interface. Theoretical equation for the membrane potential and salt flux based on the irreverssible thermodynamics in terms of the ionic mobility and effective charge density were derived by Toyoshima et al.¹²²⁻¹²⁴. The effective charge density in ion exchange membranes using the Teorell-Meyer-Sievers (TMS) theory was determined from membrane potential measurements¹²⁵⁻¹²⁹

Since the relationship that lipid bilayers comprise the fundamental structure of all biological membrane, they have been the subject of numerous experimental and computational studies. As a result, membrane models of variables complexity and destination have emerged, some aiming at elucidating structural details of the bilayer membrane and other striving to mimic its functions. The motive behind the present work is to investigate the electrochemical studies of membrane activity and permeation of biologically and therapeutically relevant compounds

Structure and composition :

Various attempts¹³⁰⁻¹³³ have been made to study the structure and the model of transport processes across the biological membranes. Several models have been proposed⁶¹⁻⁷² for understanding the behaviour of the active transport and the co-transport processes in the case of artificial as well as biological membranes, for which the relevant thermodynamic parameters and the charge densities have been evaluated. Siddiqi et al.²¹⁻²², Beg et al.⁶²⁻⁶⁷ and Ansari et al.^{68-72, 125-128} have studied many model membranes and evaluated the charge densities and other parameters based on the principles of irreversible thermodynamics¹³⁰⁻¹³³.

All biological membranes despite their different functions have a common general structure. Their core is formed by a thin film of lipid and protein molecules that are held together mainly by non-covalent forces. The lipid molecules are arranged in a continuous bimolecular layer with a thickness of approximately¹³⁴ 50 Å. The lipid barrier exhibits remarkable physical properties such as low viscosity, deformability and the ability to self-seal¹³⁵.

The bilayer structure of the membrane lipids was first shown by Gorte and Grendel¹³⁶. Ten years later, Danielli and Davson¹³⁷ proposed that the lipid bilayer is sandwiched between proteins. The Danielli-Davson model was the basis of biomembrane research, until Singer and Nicolson introduced their fluid mosaic model in 1972. The fluid mosaic model describes the cellular membrane as two-dimensional, viscous solutions of lipids and proteins at thermodynamic equilibrium. The model introduced the concept of peripheral and integral proteins. The lipids and proteins were thought to organise randomly through lateral diffusion in the plane of the bilayer, but to have restricted mobility.

The fluid mosaic model still acts as the framework when considering the dynamic and fluid structure of biological membranes, but certain revisions have been made since its introduction. It is today well established that the lipid/protein bilayer

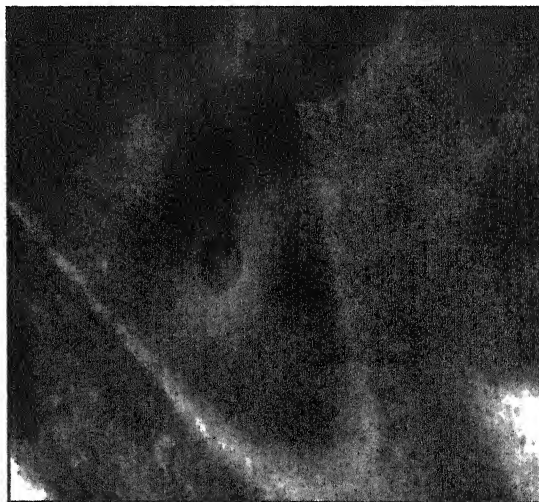
consists of lateral domains with different lipid compositions^{138,139} and that the cytoskeleton imposes restrictions on the movement of several membrane proteins^{140,141}.

TEM investigation of hen egg (*Gallus saneratii*) shell membrane:

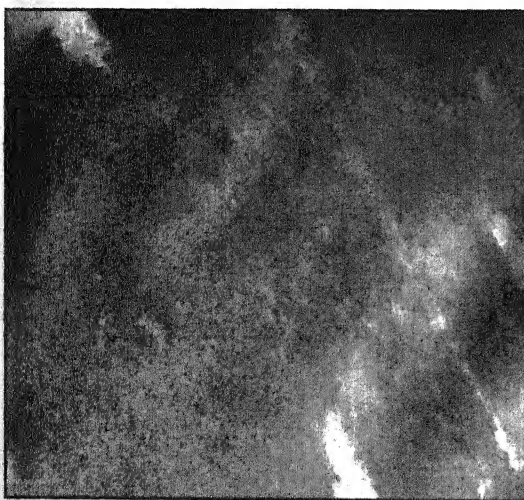
The transmission electron microscopy (TEM)- model morgagni 268D, (The Netherlands), investigation was carried out on hen egg shell membrane for structural characterisation and elucidation. The information obtained from TEM indicates that the membrane contains grater amount of protein as compared to lipids and very little carbohydrate. The TEM images are given in Figs. (3.6 a-j)



(a)



(b)



(c)



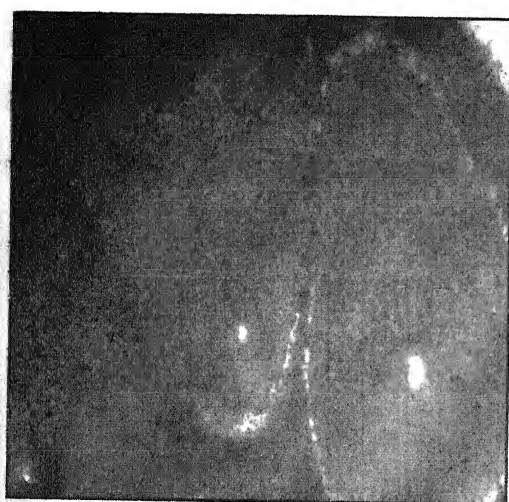
(d)



(e)



(f)



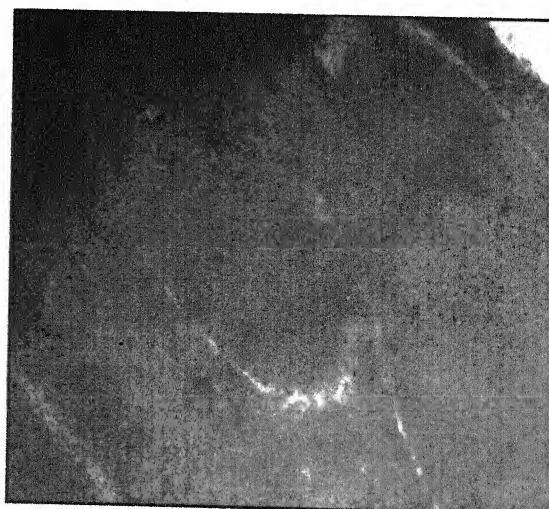
(g)



(h)



(i)



(j)

Fig. 3.6 (a-j)

Transmission electron micrographs (TEM) of hen egg (*Gallus saneratii*) shell membrane

FTIR studies of hen egg (*Gallus saneratii*) shell membrane :

The FTIR studies on hen egg (*Gallus saneratii*) shell membrane has been carried out first time to explore the exact structure. Hen egg shell membrane was isolated from the freshly laid hen egg. To carry out FTIR measurements, sample membrane was ground with dehydrated KBr in powder form, and then pellets were formed using 10 tonn hydraulic press. These pellets were used to record FTIR spectra in % Transmission mode.

The FTIR spectra were recorded on Perkin-Elmer instrument-model spectrum BX series (USA) in the region $200-4400\text{ cm}^{-1}$. The FTIR spectra for hen egg shell membrane has been displayed in Fig. (3.7) by the blue spectra. The sample spectra has also been compared with Fluka library to find out possible structure of semi membrane as displayed in the same Fig. (3.7) by red spectra.

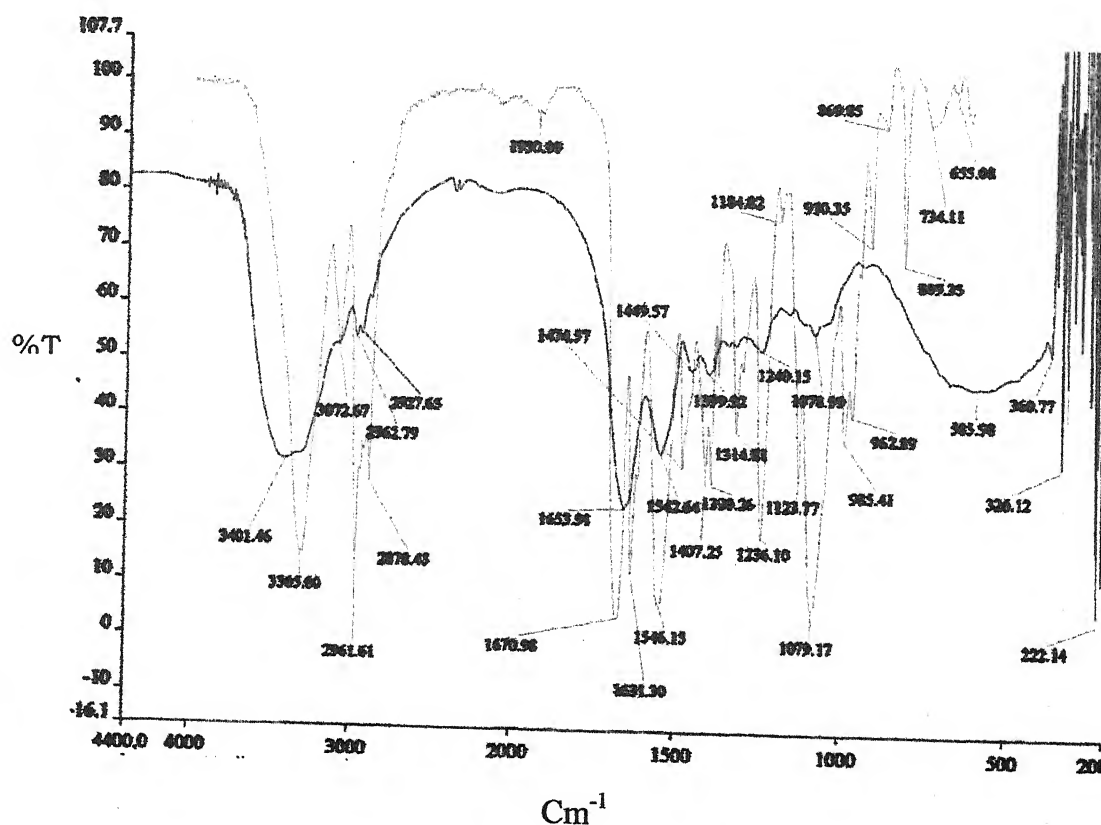


Fig. 3.7

FTIR spectra of hen egg (*Gallus saneratii*) shell membrane

for comparison it has been found that it shows the similarities with following compounds with percentage probability given in Table 3.3. Peak table with % transmission has also been given in Table 3.4

Table 3.3

Percentage structural probability of the hen egg shell membrane

% Probability	Compound
0.927	N- (Isobutoxymethyl) Acrylamide
0.921	N- Methylmercapto acetamide
0.918	D- Panthenol
0.833	Chitin
0.812	1- Formylpyrrolidine
0.784	Kappa- Carra geenan
0.753	2- -L-L- Leucine
0.734	Enzacryl poly acetal

Table 3.4

Peak table with % transmission of hen egg shell membrane

Peak No.	Wave number (cm ⁻¹)	% Transmission
1	3401.46	31.87
2	2962.79	54.41
3	1653.91	24.01
4	1542.64	33.93
5	1399.92	48.55
6	1240.15	52.77
7	1078.59	55.99
8	585.98	46.56

The above study shows that the hen egg shell membrane has the presence of IR active bands. The TEM and FTIR studied will be helpful to assign the internal structure and composition of the membrane.

Lipid Composition :

Most cell membranes are composed of approximately 50w-% lipids and 50w-% proteins. The hen egg (*Gallus saneratii*) shell membrane under investigation has been found to contain 60w-% Proteins, 45 w% lipids and about 5 w% carbohydrates. The lipid composition is always heterogeneous, including lipids with a predominantly structural role such as cholesterol and the phospholipids, as well as functional lipids like the glycolipids. In addition, membranes of animal cells contain substantial amounts of neutral lipids and free fatty acids, which are important metabolic intermediates^{135,142}. The cell membrane is basically a line-up of lipid molecules in the form of a bilayer, which is held together solely by the hydrophilic- hydrophobic forces between the lipids and the aqueous phase. This basic concept of cell membrane is now accepted, although additional factors are needed to explain real membranes (Fig. 3.8).

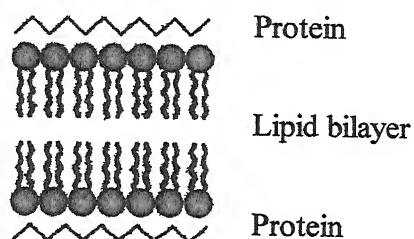


Fig. 3.8

A phospholipid bilayer

The phospholipids constitute more than half of the total lipid mass in most cell membranes. They can be divided into five classes : phosphatidylcholines (PC), Phosphatidylethanolamines (PE) phosphatidylserines (PS), Phosphatidylinositols (PI), and sphingomyelins (SPHM). phospholipids and glycolipids are commonly characterised by the structural features of their head groups (chemical composition, charge), their polar backbone (glycerol, sphingosine) and their hydrocarbon chains (number of chains, number of carbons/chain, chain saturation). The various combinations of these constituents result in the existence of thousands of different biological lipids, several hundred of which are present in the same membrane¹³⁵ Fig. (3.9) shows the structure of one of the most abundant phosphatidylcholines in biological membranes, dipalmitoyl phosphatidylcholine (DPPC).

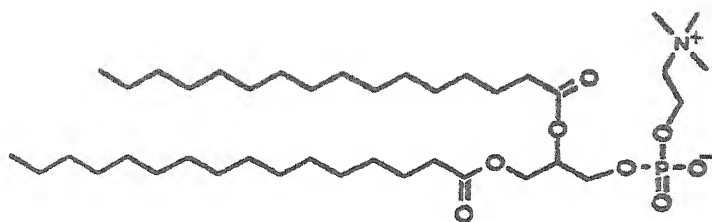


Fig. 3.9

Structure of DPPC, dipalmitoyl phosphatidylcholine.

Different mammalian cells exhibit a remarkably similar plasma membrane lipid composition, characterised by a by a high content of structural lipids. Small but significant differences in composition exist between the various membranes of a cell¹⁴². The glycolipids, for example, can be found almost exclusively in the plasma membrane, where they contribute to the negative surface charge of the cells. Phosphatidylcholines abound in the membranes of the nucleus, the mitochondria and the endoplasmatic reticulum. In comparison with other cellular membranes, the mitrochondrial membranes carry a significantly higher content of charged lipids (19-25w-%)

Differences can also be found in the distribution of fatty acid between the various types of phospholipids. Phosphatidylcholines are mainly short sphingomyelins, on the other hand, are long chain lipids (C24) with none or one double bond. The remaining phospholipds (PE, PS, PI) are characterised by their high content of polyunsaturated chains¹⁴².

Phase Behaviour :

Lipids, such as many other rod-shaped organic molecules, exhibit thermotropic polymorphism, i.e. instead of undergoing a rapid transition from solid to liquid, they pass through intermediate phases as they are heated. These mesophases are known as the liquid crystalline phases. In contrast to liquids, molecules in the liquid crystalline phases exhibit orientational order¹⁴³. The most common mesophases of lipid bilayers are the fluid L_{α} - phase, the gel-phases

P_{β}' (rippled, tilted), L_{β}' (tilted) and L_{β} (untitled), and the crystalline phase L_C ¹⁴⁴.

The crystalline L_C - phase is formed by most phospholipids at low temperatures or hydrations and exhibits both short and long-range order in three dimensions. In the presence of water, many lipids form gel phases at low temperatures. Their chains are still ordered in the all trans conformation but they undergo hindered rotations around their long axis. The gel \rightarrow fluids phase transition, also called the main or the chain melting transition, brings the hydrocarbon chains to a disordered state. Lipids in the fluid phase occupy an average molecular area of the order¹⁴⁵ of 0.65 nm^2 .

The biological lipid/protein bilayer is predominantly in a fluid state under physiological conditions. This is essential for cell growth to take place and for migrating cells (e.g. erythrocytes) to be able to travel through narrow body channels without losing their impermeability¹⁴⁵. Bilayer softness is also important to membrane spanning proteins, as the functions of many of these involve conformational changes. In order to preserve the optimal fluidity of their cell membranes, many organisms are able to adjust their lipid composition in response to changes in environmental parameters, such as temperature. This type of behaviour has been found in bacteria like *Bacillus stearothermophilus*¹⁴⁶ and *Escherichia coli*¹⁴⁷, but also in synaptic brain membranes of vertebrates¹⁴⁸.

Lateral and Transverse Order :

The lipid-protein bilayer is not a structureless fluid, but exhibits certain lateral order. The formation of lateral domains is a result of interactions between the different molecular species in the lipid/protein bilayer. Domain formation can, for instance, be driven by the co-existence of lipids in different phases¹⁴⁹ or hydrophobic mismatch of lipids with considerably different chain lengths¹⁵⁰. Another reason for domain formation is lipid- protein interactions, which can cause lipid sorting by hydrophobic matching¹⁵¹, as illustrated by electrostatic

interactions¹⁵². Domain formation can furthermore be induced and affected by external substances, such as polyelectrolytes¹⁵³ peptides¹⁵⁴ and anaesthetics¹⁵⁵.

The lateral heterogeneity of lipid bilayers and the connectivity of the membrane domains have important consequences for the functions of the cell membrane. The presence of domains has been reported to affect enzyme activity¹⁵⁶ and protein binding to the membrane surface¹⁵⁷ as well as to play a part in cell division and membrane biogenesis¹⁵⁸. Simons and Ikonen¹⁵⁹ recently proposed the existence of a particular type of microdomain, composed mainly of sphingolipid and cholesterol. These so called rafts are believed to play an important part in the sorting and transport of lipids and proteins, as well as in signal transduction¹⁶⁰.

Various experimental and theoretical studies have mapped the transverse structure of phospholipid bilayers^{161,162}. The lipid head groups are thought to lie predominantly flat on the membrane surface. The hydrocarbon chains are highly ordered in the vicinity of the polar head groups, but the order diminishes the farther away from the head group one moves (Fig. 3.10).

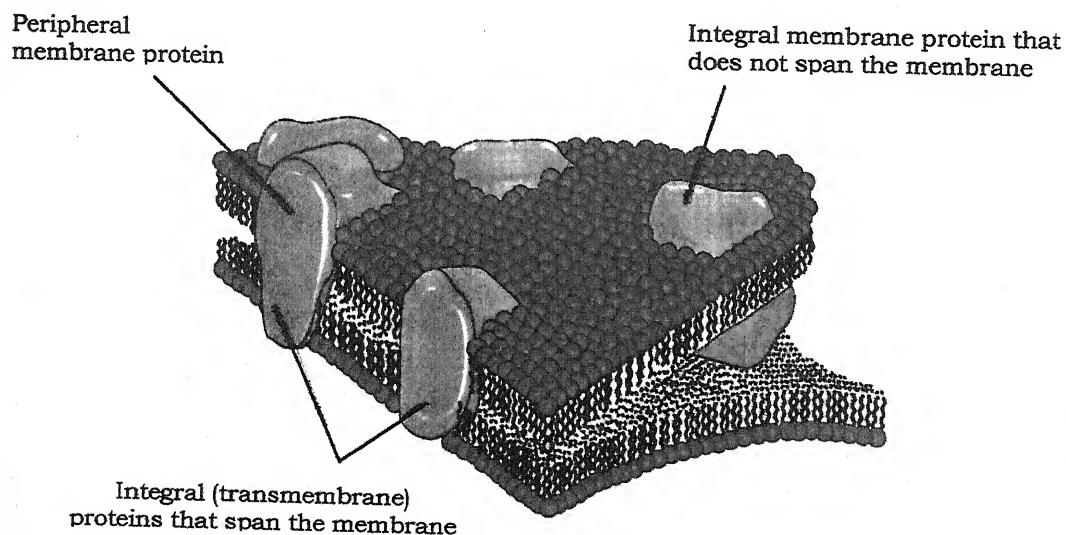


Fig. 3.10

Drawing of lipid sorting by proteins. The hydrophobic matching principle implies that the lipid species that best matches the hydrophobic length of the protein will accumulate at its periphery, adapted from Biophysical Society.

Electrical Properties :

The transverse structure of the bilayer causes the charged and dipolar lipid groups to be relatively fixed with respect to their orientation and location from the bilayer center. Consequently, these charges and dipoles are only partially compensated by water dipoles and solution electrolytes, and a complex electric profile is generated over the membrane. This profile is composed of two components: the surface, or double layer potential (Ψ_s) and the dipole potential (Ψ_d). In biological membranes, a further contribution to the electric profile is provided by the transmembrane potential differences ($\Delta\psi$). The three electric potentials are schematically illustrated in Fig. (3.11).

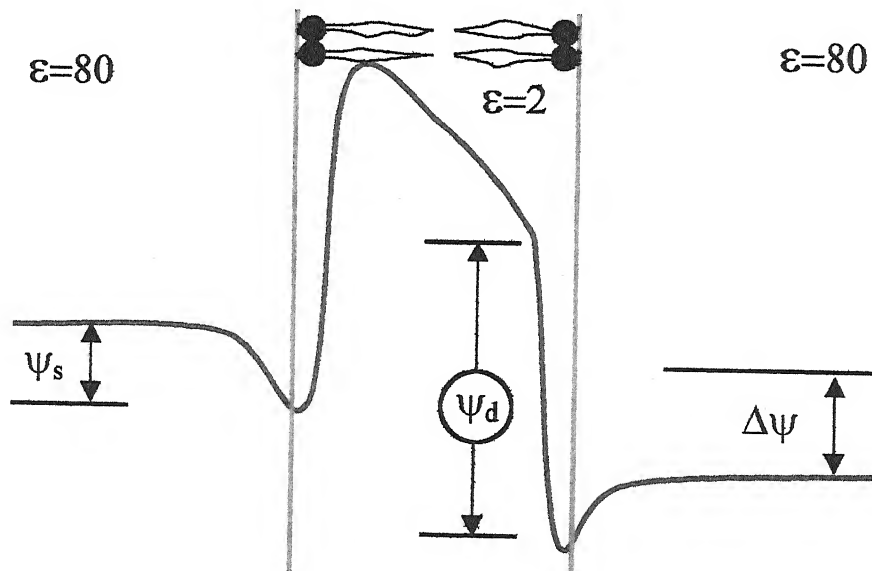


Fig. 3.11

Schematic representation of the electric potential profile across a phospholipid bilayer showing the contributions of the surface potential (ψ_s), the dipole potential (ψ_d) and the transmembrane potential difference ($\Delta\psi$), adapted from Clark¹⁶⁸.

The Surface Potential :

The surface potential profile, i.e. the potential difference between the membrane surface and the bulk aqueous phase, is commonly modeled with the classical Poisson-Boltzmann (PB) approach. The main difference between the various PB- based models

is the treatment of the spatial distribution of the counterions. The simplest model is the Gouy- Chapman (GC) theory for the diffuse layer. In the GC theory, the membrane-water interface is treated as an infinitesimally thin surface onto which the lipid charges are uniformly smeared. The surface charge is counterbalanced by a diffuse layer of solution ions, which are modeled as point charges. According to the GC theory, the relationship between the surface charge density σ and the surface potential (Ψ_o) for a system with several ionic species present is as follows :

$$\sigma = \text{sgn}(\Psi_o) \sqrt{2\epsilon_w kTN \sum_i c_{i,b} \left[\exp\left(\frac{z_i e \Psi_o}{kT}\right) - 1 \right]} \quad (3.1)$$

where ϵ_w is the dielectric permittivity of water and $c_{i,b}$ is the bulk concentration of ionic species i .

It is well known that for large surface potentials, the GC treatment of ions as point charges results in unrealistically high ionic concentrations close to the membrane surface. The GC theory furthermore ignores the possibility of any chemical interactions between the ions and the surface. Stern modified the GC theory to account for the finite-size effect of the solution ions and the possibility of chemical binding. In the Gouy-Chapman-Stern (GCS) model, planes of closest approach are assigned for the first layers of bound and non-specifically adsorbed ions. Beyond these layers, the ionic distribution follows the Gouy-Chapman picture of a diffuse layer based on point charges.

While the GCS model is clearly an improvement to the Gouy-Chapman theory, its picture of the surface structure differs significantly from that of a lipid membrane. A bilayer surface is neither homogeneous nor impenetrable, as portrayed in the GCS model. Molecular dynamics simulations indicate the thickness of the interfacial region of a DPPC bilayer to be over 1 nm^{163, 64} and the width of the head group distribution at half height to exceed 0.6 nm¹⁶⁵. Small electrolyte ions are likely to associate with charged moieties of the lipid headgroups and affect the surface charge.

A common approach has been to model the bilayer surface with a GCS - based one plane model, in which chemically bound ions are incorporated with the surface and the remaining ionic distribution obeys the GC result¹⁶⁶. In this approach, the surface density of adsorbed charge, σ_a , is obtained from the combination of the Langmuir adsorption isotherm and the Boltzmann relation. In the case of competitive binding of several ionic species to one type of binding site. One obtains.

$$\sigma_a = \frac{Ne \sum_i K_i z_i c_{i,b} \exp\left(\frac{z_i e \Psi_o}{kT}\right)}{1 + \sum_i K_i c_{i,b} \exp\left(\frac{z_i e \Psi_o}{kT}\right)} \quad (3.2)$$

where N is the surface density of binding sites and K_i is the binding constant of ion i .

The dissociation equilibrium of the lipid headgroups is ignored in many of the treatments on the surface electrostatics of lipid bilayers. Even in cases where the dissociation constant of the headgroups implies negligible or complete ionization at bulk pH, it should be kept in mind that the surface concentration of protons differs from the bulk value according to the Boltzmann distribution. Consequently, the surface charge density of the lipid headgroups may be significantly different from what is expected on the basis of the bulk P^H . Successful estimates of surface potential value may be reached without accounting for the dissociation equilibrium of the lipid headgroup, when the models employed contain a large number of adjustable parameters. The deprotonation reaction may, for instance, be masked when assuming competitive binding of several ionic species. However, as demonstrated by Aguilera et al.¹⁶⁷, neglecting the dissociation equilibrium of the headgroups may lead to serious misinterpretation of experimental results.

The Dipole Potential :

The dipole potential has been attributed to the transition region between the aqueous phase and the hydrocarbon interior of the membrane¹⁶⁸. Its magnitude in a fully saturated phosphatidylcholine bilayer has been estimated to be 220-280 mV, positive in

direction of the membrane interior^{168, 169}. Bilayer dipole potentials have commonly been determined from the difference in conductance between the hydrophobic ions tetraphenylborate (TPB) and tetraphenylarsonium (TPAs), under the assumption that their hydration energies are identical (TATB assumption). Recently, it has been suggested that previous estimates should be corrected to 60-120 mV more positive due to the inaccuracy of this supposition¹⁷⁰.

The various proposals presented for the origin of the membrane dipole potential include the carbonyl residues of the lipid ester linkage¹⁷¹, the orientation of the lipid head groups and the polarized water associated with the membrane interface¹⁷² as well as the functional group dipoles of the terminal methyl groups of the hydrocarbon chains¹⁷³. The lack of direct and non-perturbative measurement techniques to determine the partial dipole moments of these regions impedes the experimental resolution of the problem.

The formulation of a theoretical model for the dipole potential is hindered by the inadequate knowledge of the interactions from which it arises. The large change in the dielectric constant over a few Angstroms to the interface further complicates the picture¹⁷². However, the development of increasingly powerful computers and calculation algorithms has brought about new ways to study lipid bilayers through detailed computer simulations. Lipid bilayers have been modeled with a variety of approaches covering different time and length scales. The three most common ones are based on mean and self consistent field theories, Monte Carlo algorithms, and molecular dynamics (MD) calculations^{174, 175}. Particularly, the highly detailed MD simulations have shed light on the contribution of interfacial water to the dipole potential. The results obtained so far should still be regarded with some caution as despite the continuous improvement of computational resources, MD calculations are still too computer costly to be able to incorporate a bulk electrolyte.

Figure (3.12) shows the simulated electrostatic potential profile across the interfacial region of a lipid bilayer and its unphysical separation into lipid and water contributions¹⁷⁵. The lipids give rise to a negative potential in the inside of the

membrane; its magnitude is dependent on the type of lipid. For the case of DPPC, the negative sign of the lipid potential suggests an important contribution of the lipid head group dipoles, as the sn-2 chain carbonyl dipole moments are oriented with the positive charge towards the membrane interior Fig. (3.9) making their contribution one of the opposite sign. The lipid potential, however, is counteracted by the dipole moments of the interfacially aligned water molecules. The orientational polarization of interfacial water is in fact so strong that it overcompensates the sum of the lipid dipole moments, thereby inverting the dipole potential to positive inside the membrane. Several other groups have confirmed this result for the case of the uncharged lipid DPPC^{164,176,177}.

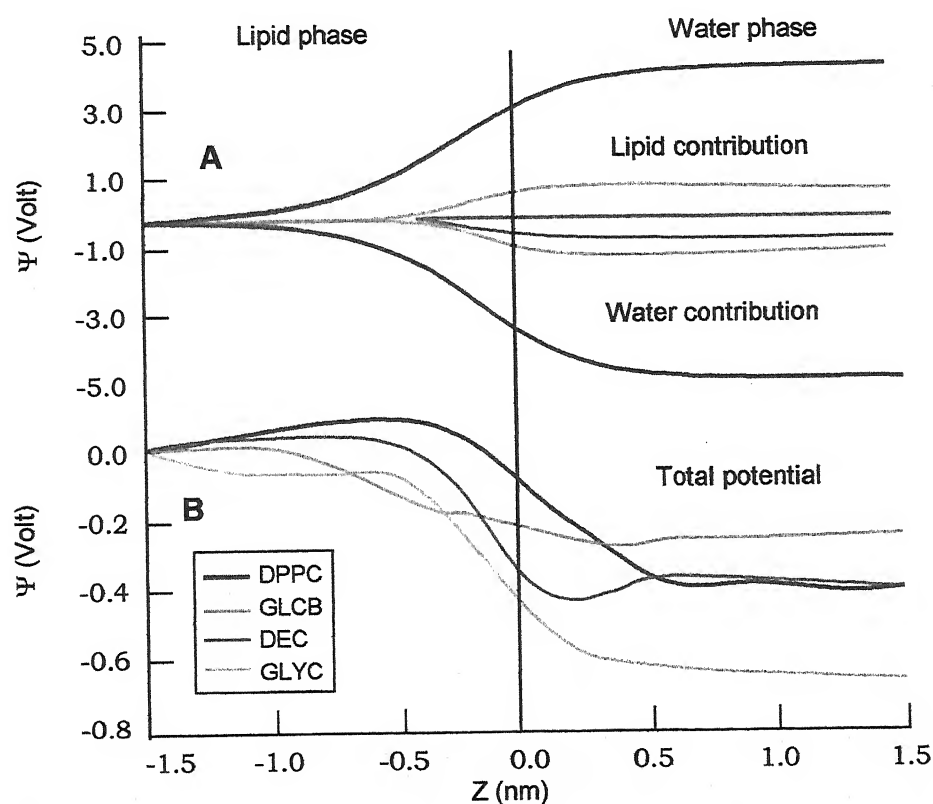


Fig. 3.12

Electrostatic potential profile across the lipid – water interface from molecular dynamics simulations. Profile are shown for three types of uncharged lipids: DPPC, β -decyl glucoside (GLCB) and dilauroyl glycerol (GLYC), and decane (DEC). (A) The upper half shows the contribution of the lipids and the lower half the contribution of the water molecules (the contribution from decane is zero). (B) The total electrostatic potential across the interface. Adapted from Tieleman et al.¹⁷⁵.

The above observation was made for lipids with zero net charge. Lopez Cascales et al.¹⁷⁸ undertook a MD study of a bilayer of negatively charged dipalmitoyl phosphatidylserine (DPPS) in the presence of counterions. They found that the headgroups charge was mainly screened by the counter ions. In addition the PS headgroups exhibited much stronger interaction with neighbouring lipids than PC headgroups, resulting in a weaker tendency to be coordinated by water. As a result, the dipolar orientation of water did not fully compensate the negative (inside) potential generated by the lipids.

The Transmembrane Potential :

The transmembrane potential, i.e. the potential difference between the intra and extracellular side of all living cells, is a result of charge separation across the membrane. It arises from the concentration gradients of certain ionic species across the cell membrane and the selective permeability of the membranes towards some of these ions. The transmembrane concentration gradients are established by active transporter proteins, which move ions across the membrane against their concentration gradient. The selective permeability of membranes is mainly due to the presence of ion channels; that allow certain ions to cross the membrane down their concentration gradients¹⁷⁹.

With regard to the transmembrane potential, it should be noted that cell membranes are classified as excitable or non-excitable. Whereas all cells respond to certain changes in their environment, excitable cells are characterized by their electrical signaling¹⁸⁰ defines cells as excitable if they express voltage - gated calcium or sodium channels. Such cells exhibit rapid changes in their permeability as a function of potential, and launch so called action potentials- the basis of electrical communication between cells. The magnitude of the transmembrane potential (at rest) depends on the cell type. Excitable cells, such as nerve and muscle cells have a resting transmembrane potential of approximately - 90 mV¹⁸⁰.

As expected, the electric potentials that are present in bilayer membranes modify the model of Berendsen¹⁸¹ in terms of permeability towards charged solutes. Surface charge and dipole density have been predicted to significantly affect the permselectivity of the bilayer towards ionic permeants, both in the case of the hydrophobic interior or the polar head group zone constituting the rate-limiting step^{182, 183}. The large and positive dipole potential makes the bilayer interior more attractive to anions than cations¹⁸⁴. In addition, the presence of a transmembrane potential difference has been found to increase ion partition into lipid vesicles¹⁸⁵.

The electric properties of biological membranes play a fundamental role in the functions of the cell. The bilayer potential profile as a whole is essential for the functions of ion channels and other protein structures. The transmembrane potential furthermore constitutes the basis of signal transduction in excitable cells. Apart from regulating the surface concentration profile of charged species, the surface potential influences a variety of membrane-related phenomena, such as phase transitions¹⁸⁶, adhesion, aggregation and fusion¹⁸⁷. Several charged lipid species are known to play a part in protein recognition and signaling¹⁸⁸. The membrane dipole potential affects the rate of transmembrane ion transport¹⁸⁷, domain behaviour¹⁸⁹ and fusion¹⁹⁰ as well as peptide insertion¹⁹¹ and enzyme activity¹⁹².

Conclusion

This chapter informs us about the structure and composition of parchment supported lead tungstate and hen egg shell biological membranes. The membranes have been characterised using SEM, TEM and FTIR techniques. The investigation reveals that lead tungstate membrane is composed of dense aggregation of somewhat larger particles and formed pores probably with non-linear channel with fully inter connected particles are irregularly condensed and

adopt a heterogeneous structure comprising masses of various size. Infrared spectra gives percentage structural probability of many similar compounds.

Hen egg shell membrane has been found to have greater amount of protein studded in the comparatively lesser amount of lipid. In the light of the above it may be hypothesized that a greater part of protein content of the membrane is devoted to pores and channels. Which are a part and parcel in the passage of ions across the membrane. Thus it is further concluded that lipid content might be providing a framework to the protein which is largely channels and pores. The infrared spectra gives percentage structural probability with similar compounds like N- (Isobutoxymethyl) Acrylamide and chitin.

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Chapter- IV

Electrochemical Theories Based on Non Equilibrium Thermodynamics

Introduction

Transport of materials across natural membranes has captured the interest of chemists, chemical engineers, and biologist. Chemist and chemical engineers would like to understand the mechanism of transport so that with knowledge so gained they would be able to fabricate membranes of any desired property or properties to be used in fuel cells, nuclear technology, desalination, nanotechnology, brakish water conversion and in many other processes. Biologists, however, would like to use artificial membranes as a simple model in order to understand the behaviour of complex biomembranes in terms of established physico-chemical principles.

Electrochemical characterisation of membranes is of vital importance from the point of view of determination of their suitability for many application of practical interest. According to schlögl¹ the current theories on the transport of charged or uncharged particles across the membrane can be roughly devided into the following groups.

Group one, considers the membrane as a surface of discontinuity setting up different resistances to the passage of the ionic or molecular species¹⁻⁴. The driving forces are the differences of the general chemical potential between the two outer media. Differences of pressure of electrochemical potential are included in the general chemical potential.

Group two, considers the membrane as a quasi-homogeneous intermediate phase of finite thickness in which the local gradients of the general chemical

potential act as driving forces⁵⁻¹⁰. Convection may also contribute to particle transport within the membrane.

Group three, considers the membrane as a series of potential energy barriers lying one behind the other, thus forming in contrast to group two an inhomogeneous intermediate phase¹¹⁻¹³. An (irregular) spatial lattice is formed due to the higher probability of finding a particle in the positions between the activation thresholds. The driving forces arise from the differences between the transition probabilities in opposite directions perpendicular to the membrane.

The theories of the first group have the advantage of being relatively simple. For ion-exchanger membranes, however, they are often inadequate. These theories deal chiefly with processes occurring within the membrane. For such a purpose the theories of the second group are proper choice.

The most important theories of the second group are based either on quasi-thermodynamics or on thermodynamics of irreversible processes. The fundamental difference between these two approaches are summarized below.

Quasi-thermodynamics is not interested in particle fluxes. One might say that the quasi-thermodynamic approach consists in taking a snapshot of the system and calculating the e.m.f from the charges which a reversible electric current would produce in the system if it were "frozen" in the state in which the photographic picture was taken. This procedure gives directly the e.m.f of the cell, no model is needed. Taking the snapshot, however, is often not as simple as it may seem. A rigorous treatment would require the knowledge of the composition of every differential layer of the diffusion zone. (i.e., the concentration profiles of all species.) Since obtaining this information experimentally is usually too lengthy a task or even quite impossible, the quasi-thermodynamic treatment is forced to make assumptions about the condition of the system.

The thermodynamics of irreversible processes¹⁴ in contrast to quasi-thermodynamics, does not require prior knowledge of the concentration profiles. The set of equations of thermodynamics of irreversible processes interrelates all occurring "fluxes" (of species electric current, heat etc.) and "driving forces" (gradients of chemical potential, electric potential, temperature, etc.). From measurements of a sufficient number of "Phenomenological coefficients", all fluxes and forces-and hence also the e.m.f. can be calculated, without knowledge of the profiles and without using the concept of "reversible energy production" on which quasi-thermodynamics is based. Furthermore, thermodynamics of irreversible processes is applicable also on the non-isothermal systems and includes coupling of fluxes which is not covered by quasi-thermodynamics.

Basic Concepts

The biological term "Permeability", taken in a narrow sense, is a quantitative measure of molecular or ionic transport, but it is often used in a somewhat wider and ambiguous way to include other phenomena related to the ionic transport, such as membrane potential, electrical conductivity etc. Any complete theory of membrane permeability ought to be able to describe all these phenomena in term of physico-chemical properties of the membrane and the nature and composition of surrounding solutions. An approach to such a theory was published by Teorell⁵. He has listed the permeability phenomena under five different headings viz. (i) ionic transport flux (ii) membrane potential (iii) electrical conductivity (iv) ionic distribution equilibrium. (v) spatial distribution of the ions and the potential within the membrane.

A characteristic property of chemically inert membranes is their ability to affect the transport of material from one side to another. Consequently the thrust of theoretical description has been the interpretation or explanation of transport processes and the measured effects resulting from pressure difference,

temperature difference, activity difference, potential difference developed across membranes and currents through membranes. A number of theoretical approaches have been given, an account of which is summarized below :

1. Irreversible Thermodynamic Approach :

At the most general and abstract level, without regard to the structure or chemical features of a membrane, the flux of matter and energy can be found in terms of the "forces" due to a pressure, temperature, activity, or potential difference across thin (or differential) membranes. The gross thermodynamic "forces" are written as :

$$X_K = -T\Delta(\bar{u}_K/T); X_u = -(1/T) \quad (4.1)$$

the material flux of each species $i = 1$ through k is

$$J_i = \sum_k L_{ik} X_k + L_{iu} X_u \quad (4.2)$$

and the flux of energy is

$$J_u = \sum_k L_{uk} X_k + L_{uu} X_u \quad (4.3)$$

The proportionality factors between each partial flux contribution and the forces are the set of Onsager¹⁵ coefficients, which are equivalent to system response functions and :

$$L_{ik} = L_{ki}; L_{iu} = L_{ui} \quad (4.4)$$

For a symmetric set of n equations with n forces, there are only $1/2n(n+1)$ independent coefficients, rather than n^2 . These forces are not arbitrarily defined but are deduced from the general expression or entropy production (rate of change of the system entropy) as the system approaches equilibrium.

A most comprehensive experimental and theoretical treatment of transport across membranes using the irreversible thermodynamic analysis is that by Mears, Thain and Dawson¹⁶. Their excellent quality of work is the systematic presentation of forms for the flux equations, choices of forces and fluxes in regard

to case in relating measured responses to Onsagar¹⁵ coefficients, and relations of relative friction and Onsagar coefficients. They advocate the procedure of reversion of the phenomenological equations in the form

$$X_k = \sum_i R_{ki} J_i \quad (4.5a)$$

which is closely related to the usual experimentally accessible friction coefficient model where

$$X_k = \sum_{ik} f_{ki} (\vec{V}_k - \vec{V}_i) = (J_k / C_k) \sum_{i \neq k} f_{ki} - \sum_{i \neq k} J_i f_{ki} / C_i \quad (4.5b)$$

The relative friction coefficients f_{ki} and f_{ik} are related by $C_k f_{ki} = C_i f_{ik}$ \vec{v} 's are velocities in the centre of mass reference frame and f_{ik} / C_k and f_{ki} / C_i are forces between i mol of i and i mol of k at unit velocity differences. The second part eqn. (4.5b) following from the definition of a flux of a single species as a product of a local concentration and velocity.

At constant temperature experimental values of zero current fluxes of salt and solvent are determined for unsymmetric bathing solutions. Electromotive flux of solvent is determined as are tracer diffusion coefficients. There are possible eight items of data : (1) electrical conductance, (2) ionic transport number, (3) electromotive flux, (4) salt diffusion flux, (5) volume or solvent osmotic flux, (6) counter ion tracer diffusion coefficient, (7) co-ion tracer diffusion coefficients, and (8) volume flow under hydrostatic pressure difference. From experimental fluxes of species under a given single gross thermodynamic forces, velocity terms are computed. The resulting matrix of unknown f values are solved using reciprocal relations and assumptions such as zero friction coefficient for tracer motion among ions of its own kind, zero friction coefficient for permselective ions interacting with matrix sites, or Spiegler's^{17,18} assumption that friction between cations and anions in a permselective ion exchanger membrane is zero. R_{ki} values are computed from f values using eqn. (4.5b) and L_{ki} values followed

by matrix manipulations. Finally, expressions for conductivity and other measurable quantities can be expressed in terms of R's and L's.

Interpretation of L_{ki} in terms of local molecular processes is not direct. Even interpretation of L_{kk} is difficult because a single gross thermodynamic force X_k producing a flux J_k simultaneously affects all other J's. Presumably these indirect interactions can be unravelled by assuming that friction coefficients represent only interactions between a pair of flows.

Even in model systems, the basic considerations of system transport can lead to complicated mathematical descriptions. The diversity in the theoretical forms for transport phenomena, which results from simplifications made by various authors, is a particular hazard to workers in this field.

It may be mentioned here that the discipline of irreversible thermodynamics provides a precise mathematical description of the processes of transport and diffusion in membrane system. Its application to membrane processes is a natural development of the basic theory of Onsager¹⁵ which has been developed by Spiegler^{17,18}, Kedem¹⁹, Katchalsky²⁰, Caplan²¹, Mears²², Rstogi²³⁻²⁶, Kirkwood²⁷, Tien²⁸ and others²⁹⁻³⁹ in an extensive and expanding literature.

2. Chemical Engineering Approach :

Closely related methods used by theoretical chemical engineers to describe membrane transport are based on turning the Nernst-Planck^{40,41} equations of motion inside out. These equations, known as Stefan-Maxwell⁴² equations, account for the motion of the centre of mass of the membrane system and remove a source of concentration dependence that measured diffusion coefficients will otherwise show when measured in a laboratory coordinate system. For each of n mobile species in one dimensional flow,

$$\begin{aligned}
 -RT \frac{d \ln a_i}{dx} - Z_i F \frac{d\psi}{dx} - (V_i - 1/C_i) \frac{dp}{dx} &= \sum_{j=1}^n (RT/D_{ij} X_j) (\vec{V}_i - \vec{V}_j) \\
 &= \sum_{j=1}^n (RT/D_{ij} C_i) (X_j J_i - X_i J_j)
 \end{aligned}
 \quad (4.6)$$

where X_i is mole fraction, C_i is concentration, in mol/cm³, V_i is partial molar volume, V_i and V_j are observable species velocities, J 's are usual fluxes in laboratory coordinates, and D 's are Stefan-Maxwell diffusion coefficients. These equations apply to closed systems, i.e. total mass of a system including bathing solutions and membrane remains constant. Considering a fixed membrane with sites designated as species 4, a simplification is found.

$$\delta_{i4} = 1 \text{ } i=4; \delta_{i4} = 0 \text{ } i \neq 4.$$

$$\begin{aligned}
 -RT d \ln \frac{a_i}{dx} - Z_i F \frac{d\psi}{dx} + (\delta_{i4}/C_i - V_i) \frac{dp}{dx} \\
 = \sum_{j=1}^n (RT/D_{ij} C_i) (X_j J_i - X_i J_j)
 \end{aligned}
 \quad (4.7)$$

Recent examples of this approach are reported in papers by Kimizuka⁴³, Sørensen⁴⁴ and samson⁴⁵. A characteristic feature of this method, as with the entirely consistent irreversible thermodynamic approach, is the large number of transport parameters which take into account interactions among moving and static components.

3. Activation Barrier Kinetic Approach :

A third type of theory treats transport processes as barrier controlled kinetic events occurring sequentially in space within the membrane. For a series of barriers across which a continuous flux occurs, relations can be derived to express flux in terms of concentrations just inside the membrane surfaces. For n barriers of equal height and spacing one obtains the trivial result :

$$J = \frac{D}{d} (\bar{C}_1 - \bar{C}_n) = P' (\bar{C}_1 - \bar{C}_n) \quad (4.8)$$

where P' is the internal permeability, \bar{C}_1 and \bar{C}_n are the concentrations in first and n th barrier. Considering the surface processes to be determined by rate constants \vec{K} , and \bar{K} , which must be assumed to be non-zero with their ratio, \vec{K} and \bar{K} , the extraction coefficient, has been related to the apparent overall permeability,

$$P = \frac{D}{d} \left(\frac{1}{K_{ext}} + \frac{2D}{dK} \right) - 1 \quad (4.9)$$

when K_{ext} and \vec{K} are small compared with D/d , then the permeability $P=K/2$. The interesting feature of this analysis, which was later improved and generalized to include flux limitation by external concentration polarisation⁴⁶, is that the unloading rate constant, K , does not affect permeability. A small K at constant \vec{K} simply means that the extraction equilibrium favours the membrane. The advantage of the so called kinetic analysis of membrane transport is that it provides an overview without the introduction of specific models for forces and system functions. On the other hand, new parameters are introduced and are related to the other better known quantities.

Absolute Reaction Rate Theory :

A membrane can be thought of a series of potential barriers existing one behind the other, across which material must pass in order to cross the membrane⁴⁶. To do so, the permeating species must have a minimum amount of energy.

The theory of absolute reaction rate has been applied to diffusion processes in membrane by several investigators, Zwolinski, Eyring and Reese¹³ considered the diffusion process as one of the basic phenomena for sustaining the growth and development of plants and organisms. They presented a detailed kinetic approach to diffusion which clarifies much established concepts and provide impetus to a fresh approach to the problems in the field of biological diffusion. The absolute

reaction rate treatment of diffusion and membrane permeability provides a general unified point of view applicable to systems of varying degrees of complexity. It is equally adoptable to the treatment of the permeabilities of membranes to electrolytes, to non electrolytes, under the driving forces of a concentration gradient, activity gradient, and external and internal potential gradients. Zwolinski, Eyring and Reese¹³ treatise on membrane diffusion is based on the "activated state" or the "transition state" theory.

Laidler and Schuller¹² have also treated the kinetics of membrane transport under steady state conditions. They employ similar principles and express the rate constant of the overall process of surface penetration in terms of a number of specific rate constants. Various special cases are considered and discussed with reference to the experimental data. They developed flux equations for solvent and solute specially as a function of the osmotic and hydrostatic pressures across the membrane. Tien and Ting²⁸ have applied the theory of absolute reaction rates to water permeation process through bilayer lipid membranes (BLM). Tsimboukis and Petropoulos⁴⁷ determined the diffusion coefficients of alkali metal ions through cellulose membranes and discussed the results in terms of the pore structure model and Iijima et al.⁴⁸ used activation analyses for the investigation of mechanism of the diffusion of ions of simple salts through polyamide membranes. Samanta et al.^{49, 50} applied absolute reaction rate theory and studied conductance behavior of microporous membranes. Beg et al.⁵¹⁻⁵² have applied absolute reaction rate theory and have derived various thermodynamic quantities like energy of activation E_a enthalpy of activation ΔH^\ddagger , free energy of activation ΔF^\ddagger and entropy of activation ΔS^\ddagger also the inter-ionic jump distance d , in order to investigate the mechanism of transport of simple metal ions through inorganic precipitate membranes.

4. Phenomenological Equation of Motion Approach :

The fourth and widely applied theory of transport is based on the Nernst-Planck flux equation⁴⁰⁻⁴¹. In its most general form, it is consistent with irreversible thermodynamic flux :

$$J_i = \bar{C}_i \bar{V}_w - \bar{D}_i \frac{\partial \bar{C}_i}{\partial x} + \bar{C}_i \frac{\partial \ln \bar{\gamma}}{\partial x} + Z_i \frac{F}{RT} \bar{C}_i \frac{\partial \psi}{\partial x} + \frac{\bar{C}_i}{RT} \left(V_i - \frac{M_i}{M_w} \bar{V}_w \right) \frac{\partial \bar{P}}{\partial x} \quad (4.10)$$

where

$$\bar{V}_w \sim d_w \left(\bar{W} F \bar{X} \frac{\partial \psi}{\partial x} - \frac{\partial \bar{P}}{\partial x} \right)$$

is the solvent transport velocity for a membrane containing sites. In its most simplified form the Nernst-Planck equation for a single ion is

$$J_i = \bar{D}_i \frac{\partial \bar{C}_i}{\partial x} - Z_i \frac{\bar{D}F}{RT} \bar{C}_i \frac{\partial \psi}{\partial x} \quad (4.11)$$

This form is the usual starting place for calculation of concentration, field and potential profile within a membrane. Current densities in the absence of interaction between species viz., ion pairing etc. are given by

$$I = F \sum_i Z_i \bar{J}_i - \left(\frac{\partial^2 \psi}{\partial x \partial t} \right) \quad (4.12)$$

Time dependence follows from continuity condition

$$\frac{\partial \bar{C}_i}{\partial t} = \frac{\partial J_i}{\partial x} \quad (4.13)$$

The second term of eqn. (4.10) is a form of Poisson's equation which for space charge build up at the surface due to current flow. Use of Nernst-Planck equations in steady state uniform (constant composition) electrolytes leads to all of the classical transport relations.

Several milestones in the application of the standard form of the N-P equation and in the interpretation and modification of the N-P equation must be mentioned. The first is an integration to give membrane potentials in terms of

external ionic activities, the historic Teorell-Meyer-Sievers equation^{5,6}, which describes the membrane potential for an ion exchanger membrane bathed in uni-univalent electrolyte of different activities. Their results include the site concentration specifically and allows for co-ion transport. It covers the range from high site densities, permselective membrane to site free membranes. No account is taken of possible solvent transport. Subsequently, Scatchard⁵³ derived an expression for the membrane potential, again for uni-univalent electrolytes, which included an integral involving transport of solvent.

The most extensive study of techniques, based on Pleijels procedure for integration of the standard Nernst-Planck equation system applicable to liquid junctions and ion exchange membranes is by Schlögl¹. His integration procedure gives the diffusion potential in terms of the fluxes and interior surface concentrations, and it gives fluxes in terms of interior diffusion potential and interior surface concentration, without the consideration of solvent transport. The method while complicated, is quite general and applicable to system involving ions of various charge. Simplification are possible when ions fall into mono groups, all ions have the same absolute charges. Schlögl's¹ subsequent papers are concerned with solutions for species flux, diffusion potentials, and current-voltage curves when solvent transport is included in the modified Nernst-Planck equation⁵⁴. A comprehensive account of Nernst-Planck flux equation is available in the book by Lakshminarayanaiah^{46,55} and in recent review by Buck.⁵⁶

This grouping attempt to classify the various mathematical approaches, according to ideal model on which they are based. It is in fact too schematic, as many theories occupy intermediate position. No author is likely to take the view that one of these treatments is right and the others wrong. The various descriptions supplement each other, and depending on the system under consideration, one of these will prove the most suitable.

Membrane Potential

A Potential difference is generally established between two electrolyte solutions at different concentration separated by an ion-permeable membrane. This potential difference, called the membrane potential, plays an important role in electrochemical phenomena which occur in biomembrane systems.

Some important theories are given for the evaluation of membrane charge density based on the thermodynamics of irreversible processes.

1. Fixed Charge Theory of Teorell-Meyer-Sievers (TMS) :

The earliest efforts towards developing a membrane model was by Michaelis⁵⁷, who considered that the charge on the membrane was due to adsorption of one kind of ion, later Teorell⁵, Meyer and Sievers⁶ developed a theory of membranes with charges fixed in the lattice. In the TMS theory there is an equilibrium process at each solution- membrane interface which has a formal analogy with the Donnan equilibrium in addition, there is an internal salt diffusion potential which was first represented by the Henderson⁵⁸ equation and later the more nearly correct Planck expression by Goldman⁵⁹. Further assumptions made are (a) the cation and anion mobilities and fixed charge concentration are constant throughout the membrane phase and are independent of the salt concentration and (b) the transference of water may be neglected. The implications of these assumptions have been discussed by Hills, Jacobs, and Lakshminarayanaiah⁶⁰.

In order to use the graphical method of Meyer and Sievers⁶, a further assumption must be made that the activity coefficient of the salt is the same in the membrane and solution phase at each interface. The introduction of activities for concentrations can only be correctly made for the Donnan potential. The expression for the diffusion potential using either the integration of Planck or Henderson equation.

According to TMS theory, the membrane potential E_m in millivolts (applicable to a highly idealized system) is given by the equation at 25°C.

$$E_m = 59.2 \left[\log \frac{C_2 (\sqrt{4C_2^2 + \bar{X}^2} + \bar{X})}{C_1 (\sqrt{4C_1^2 + \bar{X}^2} + \bar{X})} + \bar{U} \log \frac{(\sqrt{4C_2^2 + \bar{X}^2} + \bar{X}\bar{U})}{(\sqrt{4C_1^2 + \bar{X}^2} + \bar{X}\bar{U})} \right] \quad (4.14)$$

where $\bar{U} = (\bar{u} - \bar{v} / \bar{u} + \bar{v})$, \bar{u} and \bar{v} are the mobilities of the cation and the anion respectively, in the membrane phase (overbar, refer the parameters to the membrane phase). C_1 and C_2 are the concentrations of the electrolyte solution on either side of the membrane and \bar{X} is the charge on the membrane expressed in equivalents / litre.

2. Altug and Hair Theory :

Altug and Hair⁶¹ have given an ingenious and indirect method which has been developed on the lines of Teorell's model^{5,6} for the evaluation of membrane fixed charge density $\omega\bar{X}$ where \bar{X} represents the number of ionized sites per unit volume and $\omega = \pm 1$, for positive or negative membrane. According to the Teorell's model the behaviour for a charged membrane in an electrolyte solution can be characterised in terms of ionic mobilities, concentrations and fixed charge in the membrane. In TMS theory overall membrane potential was supposed to be composed of three potential jumps : two Donnan potentials one at each solution-membrane interface (here denoted by π_1 and π_2) and one residing inside the membrane the internal potential or the driving potential being denoted by $(\phi_2 - \phi_1)$. The overall total membrane potential E_{cal} is given by

$$E_{cal} = (\pi_1 + \pi_2) + (\phi_2 - \phi_1) \quad (4.15)$$

π_1 and π_2 can be calculated according to equations

$$\pi_1 = - (RT/F) \ln r_1 \quad (4.16)$$

and

$$\pi_2 = (RT/F) \ln r_2 \quad (4.17)$$

Where r_1 and r_2 are the Donnan distribution ratios at the two interfaces and are given by the equation.

$$r = \left[1 + \left(\frac{\omega \bar{X}^2}{2a} \right) \right]^{1/2} - \left(\frac{\omega \bar{X}}{2a} \right) \quad (4.18)$$

where 'a' is the external solution activity. The diffusion potential ($\phi_2 - \phi_1$) for 1:1 electrolyte is given by

$$(\phi_2 - \phi_1) = \left(\frac{u - v}{u + v} \right) \left(\frac{RT}{F} \right) \ln \left[\frac{a_1 (r_1 u + v / r_1)}{a_2 (r_2 u + v / r_2)} \right] \quad (4.19)$$

where u and v are the cationic and anionic mobilities in the membrane. However in the present calculations, these are assumed to be the same as in the bulk solutions. Subscripts 1 and 2 refer to the solutions on each side of the membrane. The use of concentration, rather than activities is an assumption based on the practical difficulty of measuring ion activities in a membrane phase as suggested by Altug and Hair⁶¹ substituting these values in eqn. (4.15) we have

$$E_{cal} = \left(\frac{u - v}{u + v} \right) \left(\frac{RT}{F} \right) \ln \left[\frac{a_1 (r_1 u + v / r_1)}{a_2 (r_2 u + v / r_2)} \right] + \left(\frac{RT}{F} \right) \ln r_2 / r_1 \quad (4.20)$$

In Altug and Hair method a value of \bar{X} was assumed and r_1 and r_2 the distribution ratio's are calculated according to eqn. (4.16-4.17) for the given electrolyte concentrations, C_1 and C_2 , the theoretical membrane potential was then determined from eqn. (4.20). By following the algebraic procedure, a series of theoretical curves were obtained for different \bar{X} values with specific electrolyte. The experimentally observed membrane potential E_m obtained were also plotted for specific electrolyte. The theoretical curve which coincided with the experimental curve gave the value of \bar{X} . In this way the value of charge density \bar{X} of any membrane can be determine.

3. Kobatake et al. Theory :

Consider a system of negatively charged membrane separating two aqueous solutions of 1:1 electrolyte having different electrochemical potentials at constant temperature. The membrane is bounded by two planes normal to the X-axis at $X=0$ and $X=L$. The fluxes of all mobile species under consideration are assumed to occur only in x-direction. The bulk solutions on both sides of the membrane are stirred vigorously to maintain uniformity of concentrations of all species in the solution phase. The density of fixed charges in the membrane is assumed to be constant and is independent of the concentrations of the external electrolyte solutions with which the membrane is in contact.

Starting with the basic flow equation provided by thermodynamics of irreversible process.^{9,14,50,60} Kobatake et al.⁶² derived the following equation for the electric current density (I)_c relative to the frame of reference fixed to the membrane.

$$(I)_c = -F(uc_+ + vc_-) \frac{dE}{dX} - RT \left(uc + \frac{d \ln a_+}{dX} - vc - \frac{d \ln a_-}{dX} \right) + F(C_+ - C_-)U_m \quad (4.21)$$

Here E is the electric potential, C_+ and C_- are concentrations of +ve and -ve ions in moles per cubic centimeter of solution, u and v are the molar mobilities of cations and anions defined in terms of the mass fixed frame of reference, U_m is the velocity of local centre of mass, R is the molar gas constant, T is the absolute temperature of system and F is the Faraday constant.

For the evaluation of U_m , the viscous force acting on 1c.c. of solution in the membrane is represented by $(1/K) U_m$ where K is a constant which is considered to depend on the viscosity of the solution and the structural details of polymer network of which the membrane is composed. The same volume of solution undergoes an electric force which is represented by

$$-F(C_+ + C_-) \frac{dE}{dX} \quad (4.22)$$

In the steady state, the sum of these two forces is zero, so that

$$U_m = -KF(C_+ - C_-) \frac{dE}{dX} \quad (4.23)$$

For convenience, Kobatake et al.⁶² have considered a membrane which is ionized negatively with a charge density \bar{X} . Then the requirement that the electric neutrality must be realized in any element of the membrane gives the relation.

$$C_+ - C_- = \bar{X} \quad (4.24)$$

Since in the system considered here no electric field is applied externally across the membrane, no net charge is transported from one side of the membrane to the other. This means that $(I)_C$ must be zero at a cross section of the membrane. Substituting eqn. (4.23) and (4.24) in to eqn. (4.21) putting $(I)_C$ equal to zero, and solving for dE/dX , the following expression is obtained.

$$\frac{dE}{dX} = \frac{-\frac{RT}{F} u(C_- + \bar{X})(d \ln a_+ / dX) - v c_- (d \ln a_- / dX)}{(u + v)c_- + u\bar{X} + KF \bar{X}^2} \quad (4.25)$$

Assumption for a_+ and a_- :

The most crucial in its derivation, is to assume that the activities, a_+ and a_- of ions in the membrane are represented by

$$a_+ = c_+; \quad a_- = c_- \quad (4.26)$$

$$\text{or } \gamma_+ = C_- / (C_- + \bar{X}); \gamma_- = 1 \quad (4.27)$$

where γ_+ and γ_- are the activity coefficients of +ve and -ve ions in the membrane.

Kobatake et al.^{63, 64} have considered a negatively ionizable polyelectrolyte gel or membrane which is immersed in a solution of a 1:1 electrolyte. At equilibrium the following relation must be obeyed.

$$(C)_0^2 = (a_+)_i (a_-)_i \quad (4.28)$$

where C_0 is the equilibrium concentration of the electrolyte in the outer solution and $(a_+)_i$ and $(a_-)_i$ are the activities of +ve and -ve ions in the gel or membrane

phase. Kobatake⁶² has assumed that the outer electrolyte solution behaves ideally, this assumption is not unreasonable. When the forms of a_+ and a_- assumed above are valid, it follows from eqn. (4.28) that

$$(C_-)_i = (C)_o \quad (4.29)$$

Applying eqns. (4.27-4.28) and using eqn. (4.29) the following relation is obtained.

$$\frac{C_o^2}{(C_+)_i (C_-)_i} = \frac{C_o}{[C_o + \bar{X}]} \quad (4.30)$$

Kobatake⁵⁹ has found that this simple relation fits well with the typical data of previous workers notably Hills et al.⁶⁰, Nagasawa et al.^{65, 66} Lakshminarayanaiah⁶⁷ and Gregor et al.^{68, 69} who determined the concentration $(C_+)_i$ and $(C_-)_i$ in ion exchange resins or membrane equilibrated with simple electrolyte solutions of given concentration C_o . Further Katchalsky et al.^{70, 71} have also pointed out the applicability of this assumption. This interesting consequence from the assumptions $a_+ = c_-$ and $a_- = c_-$ suggests that the assumed forms for the activity of small ions in polyelectrolyte gels or membranes, may have a broad applicability.

When eqns. (4.26) and (4.27) assumed for a_+ and a_- eqn. (4.25) becomes

$$\frac{dE}{dX} = - \left(\frac{RT}{F} \right) \frac{(u-v)C_- + u\bar{X}}{[(u+v)C_- + u\bar{X} + KF\bar{X}^2]C_-} \frac{dC_-}{dX} \quad (4.31)$$

when the bulk solutions on both sides of the membrane are vigorously stirred, no potential gradient is set up in them, so that the desired membrane potential E_m is obtained by integrating dE/dX over the thickness of the membrane.

$$E_m = - \frac{RT}{F} \int_0^L \frac{(u-v)C_- + u\bar{X}}{[(u+v)C_- + u\bar{X} + KF\bar{X}^2]C_-} \left(\frac{dC_-}{dX} \right) dx \quad (4.32)$$

The flow of ions and water molecules in the membrane are sufficiently slow, so that it is not unreasonable to assume that at the boundaries between the membrane and the outer electrolyte solutions, thermodynamic equilibria are established. Then eq. (4.21) holds at either membrane surface, and $C_- = C_1$ at $X=0$ and $C_- = C_2$ at $X=L$ as the boundary conditions for C_- , that are consistent with eqn. (4.32). The final expression for the membrane potential is given by

$$E_m = -\frac{RT}{F} \left[\frac{1}{\beta} \ln \frac{C_2}{C_1} - \left(1 + \frac{1}{\beta} - 2\alpha\right) \ln \left(\frac{C_2 + \alpha\beta\bar{X}}{C_1 + \alpha\beta\bar{X}} \right) \right] \quad (4.33)$$

where

$$\alpha = u/(u+v) \quad (4.34)$$

$$\beta = 1 + KF\bar{X}/u \quad (4.35)$$

and parameters have been assumed to be independent of salt concentration.

Limiting forms of Eqn. (4.20) :

Kobatake et al.⁶² have derived to useful limiting forms of eqn. (4.33).

These are :

(a) when C_2 becomes sufficiently small with v fixed : eqn. (4.33) may be expanded to give

$$|E_m^\sigma| = \frac{1}{\beta} \ln \gamma - \frac{\gamma-1}{\alpha\beta\gamma} \left(1 + \frac{1}{\beta} - 2\alpha\right) C_1 / \bar{X} \quad (4.36)$$

where $|E_m^\sigma|$ is the absolute value of a reduced membrane potential defined by

$$E_m^\sigma = FE_m / RT \quad (4.37)$$

(b) It is also been shown by Kobatake et al.⁶² that at fixed $v=10$ the inverse of an apparent transference number \bar{t}_{app} for the co-ion species in a negatively charged membrane is proportional to the inverse of the concentration C_2 in the region of high salt concentration. Here \bar{t}_{app} is defined by the relation

$$|E_m^\sigma| = (1 - \bar{t}_{app}) \ln \gamma \quad (4.38)$$

The derived transport number value has been called the apparent transport number i.e. \bar{t}_{app} because in this type of measurement water transport has not been taken into account. This apparent value will be close to the true value, when dilute solutions are used. Substituting for E_m from eqn. (4.33) and expanding the resulting expression for $1/\bar{t}_{app}$ in powers of $1/C_2$ gives

$$\frac{1}{\bar{t}_{app}} = \frac{1}{(1-\alpha)} = \frac{(1+\beta-2\alpha\beta)\alpha}{2(1-\alpha)^2 \ln \gamma} (\bar{X}/C_2) + \dots \quad (4.39)$$

Reduced Expression of Permselectivity According to Kobatake et al. :

Both the activity coefficients and mobilities of small ions in charged membranes can be expressed according to Kobatake et al.⁷² by the following expressions.

$$\gamma^+ = \gamma_+^0 (C_- \phi X) / (C_- + X), \gamma^- = \gamma_-^0 \quad (4.40)$$

$$u_+ = u_+^0 (C_- + \phi X) / (C_- + X), u_- = u_-^0 \quad (4.41)$$

Here γ_i , u_i , γ_i^0 and u_i^0 ($i=+, -$) stand for the activity coefficient and mobility of ion species i in the membrane and in the bulk solution, respectively, C_- and X are the concentration of anion adsorbed in the membrane (in moles per litre of water in the membrane), and the stoichiometric concentration of charges fixed in the membrane. According to the convention suggested by Guggenheim⁷³ γ_+^0 can be equated with γ_-^0 for 1:1 electrolyte and they are replaced by the mean activity coefficient γ_-^0 of the electrolyte component. In eqns. (4.40) and (4.41), ϕ represents the fraction of counter-ions in the unbounded form, i.e. excluding those tightly bound to the polymer skeleton constituting the membrane. ϕX may be referred to as the thermodynamically effective fixed charge density of the membrane.

Consider a system in which a negatively charged membrane is immersed in an electrolyte of concentration C . Under this condition the Donnan equilibrium for small ions holds between the membrane phase and the solution, then we have

$$(\gamma_{\pm}^0)^2 C^2 = \gamma_+^0 C_+ \gamma_-^0 C_- \quad (4.42)$$

The mass fixed transference number of anion in the membrane, τ_- is defined by

$$\tau_- = U_- C_- / (U_+ C_+ + U_- C_-) \quad (4.43)$$

Introducing eqns. (4.40), (4.41) and (4.42) into eqn. (4.43) together with the electrical neutrality condition, i.e. $C_+ = C_- + X$ we obtain

$$\tau = (1 - \alpha) \frac{\sqrt{(4\xi^2 + 1)} + 1}{\sqrt{(4\xi^2 + 1)} + (2\alpha - 1)} \quad (4.44)$$

$$\text{where } \xi = C / \phi X \quad (4.45)$$

$$\text{and } \alpha = u^0 / (u^0 + v^0) \quad (4.46)$$

on the other hand, the apparent transference number of anion in the membrane t_{app}^- is defined by the following Nernst equation

$$E_m = - (RT/F) (1 - 2t_{app}^-) \ln C_2/C_1 \quad (4.47)$$

Here C_1 and C_2 are the concentrations of the external solution in moles/litre on the two sides of the membrane and RT and F have their usual thermodynamic meaning. It has been found by Kobatake et al.⁷² that the difference between τ_- and t_{app}^- was less than 2% in the wide range of salt concentration when the average concentration $(C_1 + C_2)/2$ was replaced by C . Therefore if we replace τ_- by t_{app}^- and C by $(C_1 + C_2)/2$ eqn. (4.44) is applicable even when the concentration on the two sides of the membrane are different. Rearrangement of eqn. (4.44) leads to the equation.

$$\frac{1}{(4\xi^2 + 1)^{1/2}} = \frac{1 - t_{app}^- - \alpha}{\alpha - (2\alpha - 1)(1 - t_{app}^-)} \equiv P_s \quad (4.48)$$

Here P_s is a measure of permselectivity of the membrane electrolyte system.

4. Nagasawa Theory for Membrane Charge Density :

The system considered is a cell in which a membrane separates two aqueous solutions of different concentrations C' and C'' in moles/l. of an electrolyte. The solutions on both sides of the membrane are maintained at the same pressure and temperature. The fluxes of water and ions are expressed by the linear equations.

$$-J_0 = L_{00} \text{ grad } \bar{\mu}_0 + L_{0+} \text{ grad } \bar{\mu}_+ + L_{0-} \text{ grad } \bar{\mu}_- \quad (4.49)$$

$$-J_+ = L_{+0} \text{grad } \bar{\mu}_0 + L_{++} \text{grad } \bar{\mu}_+ + L_{+-} \text{grad } \bar{\mu}_- \quad (4.50)$$

$$-J_- = L_{-0} \text{grad } \bar{\mu}_0 + L_{-+} \text{grad } \bar{\mu}_+ + L_{--} \text{grad } \bar{\mu}_- \quad (4.51)$$

Here, subscripts +, - and o refer to cation, anion and water molecules, respectively, J's the phenomenological coefficients and μ 's the chemical potentials.

Now from eqns. (4.49- 4.51) we can obtained the following relations.

$$-J_+ = -\frac{L_{+0}}{L_{00}} J_0 + \left(L_{++} - \frac{L_{+0} L_{0+}}{L_{00}} \right) \text{grad } \bar{\mu}_+ + \left(L_{+-} - \frac{L_{+0} L_{0-}}{L_{00}} \right) \text{grad } \bar{\mu}_- \quad (4.52)$$

$$-J_- = -\frac{L_{-0}}{L_{00}} J_0 + \left(L_{-+} - \frac{L_{-0} L_{0+}}{L_{00}} \right) \text{grad } \bar{\mu}_+ + \left(L_{--} - \frac{L_{-0} L_{0-}}{L_{00}} \right) \text{grad } \bar{\mu}_- \quad (4.53)$$

Therefore, the water flow causes a term in the flux equation for each ion. In dilute electrolyte solutions, however,, Nagasawa^{74, 75} have assumed that the cross terms in eqns. (4.52) and (4.53) i.e. the third term in eqn. (4.52) and the second term in eqn. (4.53) are negligible as compared with the other term⁷⁶. Similar assumptions were assumption employed by Spiegler⁷⁷, Kedem and Katchalsky⁷⁸ for transport of ions through charged membrane⁷⁹. If the forces $\text{grad } \bar{\mu}_+$ and $\text{grad } \bar{\mu}_-$ in eqns (4.52) and (4.53) are replaced by J_+ and J_- , the following expressions are obtained

$$-J_+ = -\frac{(\bar{C}_- + \phi X)}{\bar{C}_0} J_0 + (\bar{C}_- + \phi X) u \text{grad } \bar{\mu}_+ \quad (4.54)$$

$$-J_- = -\frac{\bar{C}}{\bar{C}_0} J_0 + \bar{C}_- u \text{grad } \bar{\mu}_- \quad (4.55)$$

where \bar{C}_- is concentration of coions, and concentration of countorions may be expressed by $(\bar{C}_- + \phi X)$, where ϕX is the thermodynamically effective fixed charge density.

It is assumed that the rate-determining step for the permeation of ions and water is the mass transfer in the membrane phase and that the electrolyte solutions inside and outside the membrane are in thermodynamic equilibrium on both sides of membrane. Therefore, the effect of a stagnant layer on the permeation velocities^{80,81} is neglected. This assumption is valid for thick membrane. From the condition of no current for 1:1 electrolytes.

$$\begin{aligned}
 -F \text{ grad } E = & - \left(\frac{J_0}{\bar{C}_0} \right) \frac{\phi X}{(\bar{C}_- + \phi X)u + \bar{C}_- v} + \frac{(\bar{C}_- + \phi X)u}{(\bar{C}_- + \phi X)u + \bar{C}_- v} \text{ grad } \bar{\mu}_+ \\
 & - \frac{\bar{C}_- u}{(\bar{C}_- + \phi X)u + \bar{C}_- v} \text{ grad } \bar{\mu}_- \quad (4.56)
 \end{aligned}$$

Substituting eqn. (4.56) into eqns. (4.54) and (4.55) the following is obtained

$$-J_s = - \left(\frac{J_0}{\bar{C}_0} \right) \frac{\bar{c}_- (\bar{c}_- + \phi X) (u+v)}{(\bar{c}_- + \phi X)u + \bar{c}_- v} + \frac{\bar{c}_- (\bar{c}_- + \phi X) u v}{(\bar{c}_- + \phi X)u + \bar{c}_- v} \text{ grad } (\bar{\mu}_+ + \bar{\mu}_-) \quad (4.57)$$

equation (4.56) is rewritten as

$$-J_s = - \left(\frac{J_0}{\bar{C}_0} \right) \frac{\bar{c}_- (\bar{c}_- + \phi X) (u+v)}{(\bar{c}_- + \phi X)u + \bar{c}_- v} + \frac{(2\bar{c}_- + \phi X) u v RT}{(\bar{c}_- + \phi X)u + \bar{c}_- v} \text{ grad } \bar{c}_- \quad (4.58)$$

Performing the integration of eqn (4.58) from one side of the membrane (') to the other ("), then gives

$$\begin{aligned}
 -J_s = & \left(\frac{RT}{d} \right) \frac{2u v A_1 (A_1 - \phi X) \left(A_1 - \frac{\phi X}{2} \right)}{(u+v) (A_1 - A_2) \left(A_1 - \frac{\phi X u}{u+v} \right)} \\
 & \ln \left(\frac{\bar{c}'_- + A_1}{\bar{c}''_-} \right) + \left(\frac{RT}{d} \right) \frac{2u v A_2 (A_2 - \phi X) \left(A_2 - \frac{\phi X}{2} \right)}{(u+v) (A_2 - A_1) \left(A_2 - \frac{\phi X u}{u+v} \right)} \ln \left(\frac{\bar{c}'_- + A_2}{\bar{c}''_- + A_2} \right) \quad (4.59)
 \end{aligned}$$

where

$$A_i = \frac{1}{2(u+v)} \left[\phi X u + \frac{2RT \bar{c}_0 u v k}{J_0} + (-1)^i \left\{ \left(\phi X u - \frac{2RT \bar{c}_0 u v k}{J_0} \right)^2 + 4(\phi X)^2 u v \right\}^{1/2} \right] \quad (4.60)$$

The parameter d is the thickness of the membrane and k is a constant.

5. Aizawa et al. Theory for Membrane Charge Density :

The Aizawa et al.⁸² theory is an extended form of Nagasawa et al.^{74, 75} approaches for the evaluation of fixed charge density based on thermodynamics of irreversible processes. According to Aizawa trans-membrane potential across a charged membrane has also been approximated as

$$\left(\frac{F}{RT}\right) E_m = -\ln \gamma + \ln \frac{-\phi X + \sqrt{(\phi X)^2 + 4(c'')^2}}{-\phi X + \sqrt{(\phi X)^2 + 4(c')^2}} + (2t_- - 1) \ln \frac{(1 - 2t_-) \phi X + \sqrt{(\phi X)^2 + 4(c'')^2}}{(1 - 2t_-) \phi X + \sqrt{(\phi X)^2 + 4(c')^2}} \quad (4.61)$$

where t_- is the transport number of environment for a slightly charged membrane, i.e. when $\phi X \ll C$, eqn. (4.61) reduces to (4.62)

$$\left(\frac{F}{RT}\right) E_m = (2t_- - 1) \ln \gamma + \{2(\gamma - 1/\gamma)\} t_- (1 - t_-) \frac{\phi X}{c''} \quad (4.62)$$

which predicts a straight line plot of $\left(\frac{F}{RT}\right) E_m$ against $1/c''$ at fixed γ , and allows the evaluation of t_- and ϕX from the intercept and slope of linear plot.

Bi-ionic Potential

A study electromotive force of a bi-ionic cell containing two electrolytes AX and BX separated by a membrane is called the bi-ionic potential (BIP). This potential is a measure for or the selectivity of a membrane for the ions of the same sign and is of great interest in biology and acquire increasing interest in industrial practice.

Most probably first time the bi-ionic potential values were reported by Marshall et al.⁸³, Bernfield⁸⁴ and Sollner et al.^{85, 86}. Manecke⁸⁷ and Wyllie⁸⁸ using the Henderson⁵⁸ equation for liquid junction potential and replacing the concentrations by activities, Marshall⁸³ derived equations for the bi-ionic membrane potential theories in order to characterise the membranes. Under the studies of bi-ionic potential and confrontation with experimental results, L. Dammak and co-workers⁸⁹ carried out the theoretical study of bi-ionic potential in the case of mixed control of the inter-diffusion process and compared with experimental results in order to test the theories. Recently a number of investigators⁹⁰⁻⁹³ have also utilized biionic membrane potential theories for

characterizing the various types of the membranes with a view to establish their applications.

The mechanism of the bi-ionic potential was considered in detail by sollner^{85, 86}. He found that not only the relative mobility of the counterions was important but also the selectivity of the membrane material equally played significant role. According to his views, when the membrane is fixed in a bi-ionic cell, one ion is preferred to the same extent as the membrane is in equilibrated with mixed solution containing both counter-ions. His equation for the potential (restricted to 1:1 electrolytes), reflects the two factors relative to mobility (\bar{D}_A / \bar{D}_B) and preferential adsorption (\bar{V}_B / \bar{V}_A) by the membrane.

$$\Delta\phi = \frac{RT}{F} \ln \frac{\bar{D}_A \bar{V}_B}{\bar{D}_B \bar{V}_A} \quad (4.63)$$

Wyllie⁸⁸ combines the theories of Sollner^{85, 86} and Marshall⁸³ and uses the Henderson⁵⁸ equation (with activities) for the diffusion potential in the membrane. He also adds the Donnan potentials, and as Sollner^{85, 86} corrects for the assumed preferential adsorption by multiplying the mobility ratio with the activity coefficient ratio. His equations are, as eqn. (4.63) in accordance with those derived quasi thermodynamically.

Toyoshima et al. Theory

Toyoshima et al.^{62, 80, 94-96} have derived various equations for bi-ionic potential and membrane potential on the basis of non equilibrium thermodynamics, using the appropriate assumptions for the motilities and activity coefficients of small ions in the membrane phase. The salient features of Toyosima et al.⁹⁴ theory are described below.

Consider a system in which two large compartments contain aqueous solutions composed of two simple 1:1 electrolyte AP and BP. Here A and B represent the cationic species and P is the common anion. The system is isothermal and there is no electric field applied externally across the membrane. The electric charge carried by the membrane matrix are negative charges and distributed uniformly with a charge density \bar{X} . The solutions are so vigorously stirred that the concentration in each of the compartments is maintained uniformly. The flow of all components in the membrane is considered to occur only in the direction of membrane thickness. Neglecting interacting flows between ions of different species and the effect of mass flows, the fluxes of ions A, B and P are given by

$$J_N = -U_N C_N (RT d \ln a_N / dx + F d \phi / dx) \quad (4.64)$$

$$(N=A,B)$$

$$J_P = -U_P C_P (RT d \ln a_P / dx + F d \phi / dx) \quad (4.65)$$

where J_i ($i = A, B, P$) is the flux of ionic species i relative to the frame of reference fixed to the membrane. v_i , C_i and A_i are the mobility (relative of the local centre of mass), molar concentration and activity of ion i . For the unidimensional flows, the law of mass conservation gives the equation, when the flows are stationary.

$$dJ_i/dx=0 \quad (i=A,B,P) \quad (4.66)$$

Hence we have $J_N = \text{constant}$ with respect to axial direction. Rearranging the eqn. (4.65) the gradient of the electrochemical potential of the anion is represented in terms of J_p , A_p and $u_p c_+$ as

$$\frac{dv_p}{dx} = RT d \ln a_a dx - F d \phi / dx = -J_p / u_p c_p \quad (4.67)$$

The integration of eqn. (4.67) between two bulk solutions across the membrane leads to

$$\Delta u_p = -J_p \int_0^L (1/u_p c_p) dx = -F\Delta\phi RT \ln (a_p'' / a_p') \quad (4.68)$$

where ' and '' indicate the values in the external solutions 1 and 2. Using the steady state conditions, $J_p = \text{constant}$ with respect to x , eqn. (4.68) may be written to give

$$\Delta\phi BIP = (J_p / F) \int_0^L (1/u_p c_p) dx + \frac{RT}{F} \ln (a_p'' / a_p') \quad (4.69)$$

Where $\Delta\phi$ is the difference of the electric potential between two bulk solution. In the system of negatively ionizable membrane and a 1:1 electrolyte the following assumptions are made for the concentration of u_i and a_i of ion i ($i=+, -$) in the membrane phase⁹⁶.

$$u_- C_+ = u^0 + (C_- + \bar{X}) \text{ and } u_- c_- = u^0 c_- \quad (4.70)$$

$$a_+ = v_+^0 (C_+ + \bar{X}) \text{ and } a_- = v_-^0 c_- \quad (4.71)$$

Here u_i^0 and v_i^0 are the mobility and activity coefficient of ion i in free solution. The quantity \bar{X} is called the thermodynamically effective concentration of counter ions dissociated from the ionizable groups fixed on membrane matrix.

The system is now composed of the following four kinds of electrolytes AP, BP, AM and BM, where M represents the negatively ionizable group fixed on the membrane skeleton. The eqns. (4.70) and (4.71) applied to the system with the following assumption⁹⁶. The ratio of C_{AM} to C_{BM} is equal to that of C_{AP} to C_{BP} , i.e.

$$\frac{C_{AM}}{C_{BM}} = \frac{C_{AP}}{C_{BP}} \quad (4.72)$$

and electrical neutrality is main in any element of the membrane, so

$$C_{AM} + C_{BP} = \bar{X} \quad (4.73)$$

The expressions for the activities and the mobilities for small ions in the membrane under above stated conditions are given by following expressions,

$$\begin{aligned}
a_A &= C_{AP} [1 + \bar{X} / C_{AP} + C_{BP}] \\
a_B &= C_{BP} [1 + \bar{X} / (C_{AP} + C_{BP})] \\
a_p &= C_{AP} + C_{BP}
\end{aligned} \tag{4.74}$$

and

$$\begin{aligned}
u_A C_A + u_A^0 a_A \\
u_B C_B = u_B^0 a_B \\
u_P C_P = u_P^0 a_P
\end{aligned} \tag{4.75}$$

Where C_{AP} , C_{BP} , C_{AM} and C_{BM} are the concentrations of the electrolytes AP, BP AM and BM respectively.

Equation (4.69) for the bi-ionic potential may be rewritten in the following form

$$\Delta\phi_{BIP} = \frac{RT}{F} \left[\ln \left(\frac{\epsilon_L + \eta_L - 1}{\epsilon_0 + \eta_0 - 1} \right) - (2J - 1) \ln \left(\frac{\epsilon_L + \eta_L - J}{\epsilon_0 + \eta_0 - J} \right) \right] \tag{4.76}$$

where ϵ_0 and ϵ_L are the values of ϵ in the membrane phase at $x=0$ and $x=L$ and η_0 and η_L are the corresponding values of η . The term ϵ and η are the reduced concentrations defined by $\epsilon = (C_{AP}/\bar{X}) + C_{AP} / (C_{AP} + C_{BP})$ and $\eta = (C_{BP}/\bar{X}) + C_{BP}/(C_{AP} + C_{BP})$

By taking the assumption, that at both membrane surfaces the equilibrium distribution of every ion species is maintained between the membrane phase and external bulk solution⁹⁶ and also neglecting the effect of osmotic pressure produced between the two phases, the following expression are obtained.

$$\begin{aligned}
K_N^2 (a_{NP})_I^2 &= (a_N)_0 (a_p)_0 \\
K_N^2 (a_{NP})_{II}^2 &= (a_N)_L (a_p)_L
\end{aligned} \tag{4.77}$$

where $(a_{NP})_I$ and $(a_{NP})_{II}$ are the mean activities of the electrolytes NP ($N=A, B$) in both solutions I and II respectively, defined by

$$\begin{aligned}
(a_{NP})_I^2 &= a_N^I a_p^I \\
(a_{NP})_{II}^2 &= a_N^{II} a_p^{II}
\end{aligned} \tag{4.78}$$

$(a_i)_0$ and $(a_i)_L$, ($i=A,B,P$) are the single ion activities of species in the membrane phase at $x=0$ and $x=L$ and K_N ($N=A, B$) is defined by

$$1/K_N = \exp \left[\left(\mu_N^{0m} - \mu_N^{0b} + \mu_P^{0m} - \mu_P^{0b} \right) / 2RT \right] \quad (4.79)$$

In eqn. (4.79) μ_n^{0m} is the standard chemical potential of cation in the membrane phase and μ_N^{0b} is that in external bulk solution and μ_p^{0m} and μ_p^{0b} are the corresponding values of anion P.

By solving various equations, Toyoshima et al.⁹⁶ gave the equation for BIP in the following form

$$\Delta\phi_{BIP} = \left[2 \ln \left(\frac{K_A}{K_B} \right) - \ln \left(\frac{JV_A + 1}{JV_B + 1} \right) \right] (F/RT) \quad (4.80)$$

This equation is used for the determination of theoretical values of BIP for model and biological membranes.

Apart from various theoretical treatments used in the investigation of membrane systems, one of the most important approaches in membrane studies is the application of electrochemical principles. Electrochemistry in membrane studies is pertinent at three levels⁵⁶. One is the development of techniques with application to experimental phenomenology including current-voltage-time-concentration behaviour. A second is mathematical modelling implied by experiment and tested against experiment. The third level is experimental verification of models in terms of the molecular processes and properties and includes determination of theoretical parameters by electrical methods and by complementary non-electrochemical methods: physical, optical, ESR, NMR, DSL, LB, FTTR, XRD, TEM, Zetasizer and T-jump technique etc. From transient and steady state measurement of current or membrane potential as a function of chemical composition, chemical treatment, and temperature, the roles of kinetic and equilibrium parameters can be deduced or inferred. A possible approach to

modeling begins with the assumption of the membrane as a linear system to which laws of network theory may be applied. Another begins by solution of basic electro-diffusion laws of transport with equilibrium or kinetic boundary conditions in order to deduce forms for system functions which satisfy the data.

The most important contribution of electrochemists to membrane electrochemistry is the transfer of perspective and wisdom to the new area. There are many sine qua nons in electrochemistry which have occurred through extensive studies of electrolytes and electrolyte/membrane interfaces. Electrochemists have learned to sub-divide systems into interfacial and bulk processes and to expect effects of dielectric constant (complex formation, ion pairing.), effects of short range forces (adsorption of charged and uncharged species with, possible, changes in rates of interfacial processes), effects of high field near surfaces (wien effect, and dielectric saturation, for example), and the important effect of local potentials on rates of interfacial processes (irreversible charge transfers, psl effects, etc.). In as much as the presence of the space charge at interfaces is a natural consequence of the continuity of potential from one phase to another, the presence of space charge and space charge mediated effects in membrane systems is anticipated.

The success attending any unit operation in which membranes form an integral part, such as demineralisation by electrolysis, salt filtration by application of pressure, etc. depends on the availability of suitable membranes. The suitability of membrane for any particular operation is determined by a number of factors. A very important requirement is that the membrane should be chemically stable when immersed in salt solutions of various pH and in salt solutions containing solvents or oxidizing agents and should never become fouled by surface agents or detergents likely to be present in solution to be employed with membranes. Besides this chemical stability, it should have some mechanical

strength and low electrical resistance. In addition, the membrane should have good dimensional stability under different wetting conditions. Sufficient membrane flexibility is another property which enhances membrane suitability, as it facilitates easier handling without breakage during any operation. Other desirable properties which a membrane may have to become of practical importance are: (a) high ionic selectivity even in high salt environment, (b) low salt diffusion in a membrane concentration cell, (c) low electroosmotic water transport. To "tailor make" a membrane satisfying the above characteristics cells for affecting compromise between opposing requirements, considerable attention, therefore, has been paid, in recent years, to the development of membranes with particular and specific properties. A variety of compounds and processes have been used to prepare them. The basic material and the chemical processes involved are summarized in a book of A.G. Fane^{97, 98} and Kesting⁹⁹, and short introduction on the preparation of ion exchange membranes have been written by Kitchner¹⁰⁰, Kunin¹⁰¹ spiegler¹⁰², Lakshminarayanaiah^{46, 55, 102} and others.

Conclusion

Electrochemical characterisation of membrane is of vital importance from the point of view of determination of their suitability for many applications of practical interest. Electrochemical studies of biological and model membranes are totally based on certain widely accepted theories of irreversible thermodynamics. Various theoretical equation have already been derived by many workers in order to evaluate important parameters governing the membrane phenomena regarding their electrochemical characterisation. Basically various approaches are taken into account by the author for the establishment of recent theories for membrane potential, bi-ionic potential, charge density and membrane impedance etc. which rely on the characterisation of the membranes.

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Chapter - V

Transport Studies Based on Membrane Potential Measurements

Introduction

The Most important characteristics property describing membrane phenomena is the thermodynamically effective fixed charge density. Any artificial membrane, charged or uncharged, used as a barrier to separate any two phases, aqueous or non-aqueous, is active unless it is too fragile in that it exercises varying degrees of control on molecules moving across it. This ability arises from two membrane characteristics, presence of inorganic groups and 'Pores' (Space occupied by water in the case of aqueous solutions). All membranes, artificial or natural always carry inorganic groups either fixed to the three dimensional membrane matrix as observed in ion exchange membranes or adsorbed as generally seen in colloidal system.

One of the most consistent properties of biological system is the presence of a voltage across the cellular surfaces. The mechanism whereby this potential arises is still in dispute. Some consider it to be a diffusion potential while other suggest the voltage to be an adsorption potential¹. Teorell^{2,3} considered the presence of charge on the membrane skeleton responsible for the development of potential across it. Based on fixed charge concept a number of theoretical equations for membrane potential, developed across a charged membrane separating two electrolyte solutions, have been derived and tested using, generally synthetic (model) and natural membranes. However, the various attempts made to calculate membrane potentials fall into three groups: (a) the idealized theory of Teorell-Meyer-Sievers^{2,4} (TMS) and its refinements⁵, (b) the pseudo-thermodynamic approach due to scatchard and treatment based on the

thermodynamics of irreversible processes⁶ and (c) kinetic approach based on the theory of absolute reaction rate^{7,8}.

A potential difference is generally established between two electrolyte solutions at different concentration separate by an ion-permeable membrane. This potential difference, called the membrane potential, plays an important role in electrochemical phenomena observed in various bio-membrane systems. As is well known, in the stationary state the membrane potential arises both from the diffusion potential^{9,10} and membrane boundary potential¹¹⁻¹⁴.

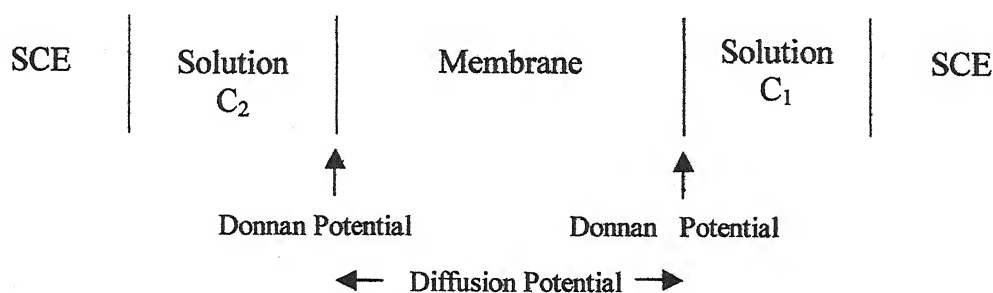
The chapter is concerned with the evaluation of effective fixed charge density of parchment supported inorganic precipitate lead tungstate model membrane and hen egg (*Gallus saneratii*) shell biological membrane, from membrane potential measurements using different theories, namely those of Teorell-Meyer-Sievers²⁻⁴ (TMS), Altug and Hair¹⁵, Kobatake et al.¹⁶⁻²⁴, Nagasawa et al.²⁵ and the theory of Aizawa et al.²⁶ based on the thermodynamics of irreversible processes. This is in order to substantiate our earlier findings, on the basis of Eisenman-Sherry model of membrane selectivity, that egg shell membrane and parchment supported membranes possess small density of fixed charge groups on the membrane matrix, as well as to test the validity of the developed theories for membrane potential.

Experimental

Parchment supported inorganic precipitate lead tungstate model membrane has been prepared by the method of interaction as suggested by Beg and coworkers^{27,28}. To precipitate these substances in the interstices of parchment paper, a 0.2M solution of sodium tungstate (S. d. Fine Ltd.) was placed inside glass tube, to one end of which was tied the parchment paper (supplied by M/S Baird and Tatlok London Ltd.) previously soaked in deionised water. The tube was suspended for 72 hours in a 0.2 M solution of lead nitrate (Ranbaxy). The two

solutions (fresh solution) were interchanged later and kept for another 72 hours. Thus parchments paper and inorganic precipitate as a whole acts as a model membrane. The membrane thus prepared was washed with deionized water to remove free electrolytes.

The egg shell membrane was isolated from the freshly laid hen egg (*Gallus saneratii*). The egg was broken first at one end. Yolk and white of the egg were poured out. The egg membrane was then separated gently from the hard CaCO_3 covering. The shell membrane consisting of two layers a thick outer next to CaCO_3 shell and a thinner next to the albumin³. The hen egg shell membrane preserved in an ice-cold Ringer solution of $\text{pH } 7.4 \pm 0.2$. The Ringer solution contained (in gm/l) NaCl , 9.00; KCl , 0.42; CaCl_2 , 0.24; glucose and NaHCO_3 , 0.15. The membrane was washed several time with deionized water to remove any traces of Ringer solution before recording the membrane potential. These membranes were then clamped separately between two half cells of the electro-chemical cell of the type :



for the measurement of membrane potential $\text{Hg-Hg}_2\text{Cl}_2 - \text{KCl}$ was used as a reference electrode. The total potential difference between reference electrode placed on either side of the membrane is the algebraic sum of the electrode potential, i.e., concentration potential and the membrane potential $E_m^{29, 30}$. A tenfold difference in concentration of chloride solutions (i.e. ; $C_2/C_1=10$) was maintained and measurements were made by a digital multimeter (Rish Multi[®] 4 $\frac{3}{4}$ digits, 18 S). The solutions were replaced by fresh solutions and when there was

no change in potential with the addition of fresh solution, with constant vigorous stirring by a pairs of magnetic stirrers, it was taken as the true total potential difference across the Hg-Hg₂ Cl₂-KCl electrodes. In all the membranes it could be reproduced within a few tenths of a mV. The whole cell was immersed in a water thermostat maintained at $25 \pm 0.1^\circ\text{C}$. The various salt solutions (chlorides of Li⁺, Na⁺ and K⁺) were prepared from BDH, AR grade chemicals and deionized water.

Results and Discussion

The values of membrane potential E_m measured across parchment supported lead tungstate membrane and hen egg shell membrane in contact with various 1:1 electrolytes are given in Tables 5.1-5.2 . These membrane potential values are plotted in Figs. (5.1-5.2) against $\log (C_1+C_2) / 2$.

Table 5.1

Experimentally observed values of membrane potential E_m (mV) across parchment supported lead tungstate membrane in contact with various 1:1 electrolytes at $25 \pm 0.1^\circ\text{C}$

Concentration (Mol/l) C_2/C_1	Electrolyte		
	KCl	NaCl	LiCl
1.0/0.1	1.41	-3.88	-15.30
0.5/0.05	3.37	-3.18	-14.63
0.1/0.01	11.33	6.03	-13.36
0.05/0.005	16.15	8.90	-6.10
0.01/0.001	30.10	20.91	12.18
0.005/0.0005	36.23	24.10	20.85
0.001/0.0001	37.78	24.23	21.65

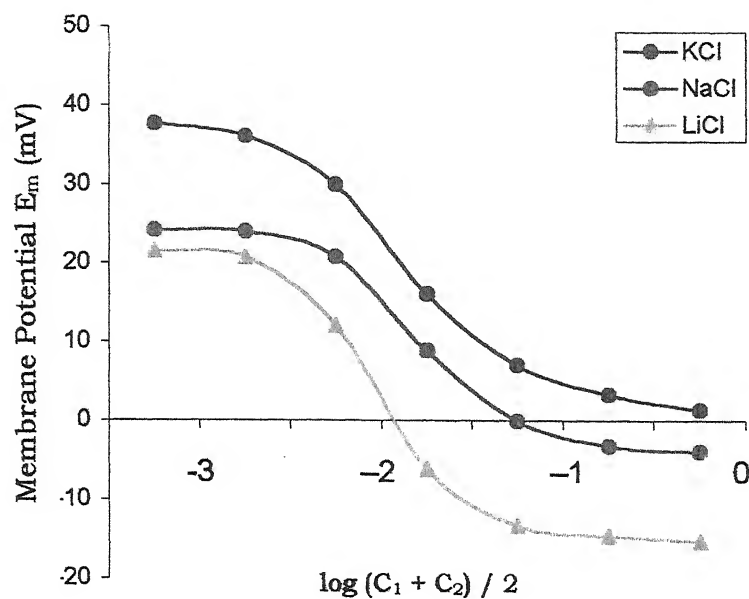


Fig. 5.1

Plots of membrane potentials E_m (mV) against $\log (C_1 + C_2) / 2$ using 1:1 electrolytes across lead tungstate membrane

Table 5.2

Experimentally observed values of membrane potential E_m (mV) across hen egg shell membrane in contact with various 1:1 electrolytes at $25 \pm 0.1^\circ\text{C}$

Concentration (Mol /l) C_2/C_1	Electrolyte		
	KCl	NaCl	LiCl
1.0/0.1	-6.4	-16.04	-20.9
0.5/0.05	-8.8	-18.09	-24.4
0.1/0.01	-14.6	-24.01	-25.6
0.05/0.005	-16.3	-29.05	-32.0
0.01/0.001	-19.5	-33.08	-33.7
0.005/0.0005	-20.4	-34.07	-35.0
0.001/0.0001	-20.6	-34.08	-35.1

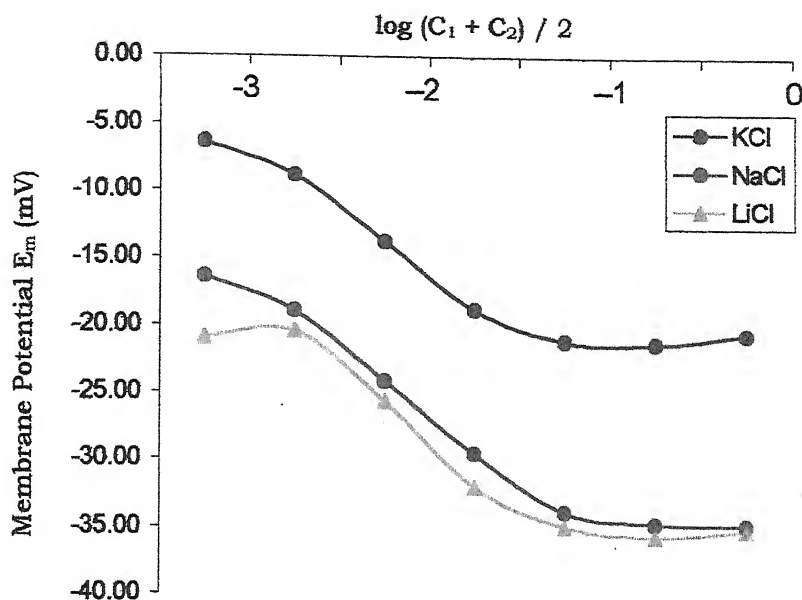


Fig. 5.2

Plots of membrane potentials E_m (mV) against $\log (C_1 + C_2) / 2$ using 1:1 electrolytes across hen egg shell membrane

When two electrolyte solutions at difference concentration are separated by a membrane the mobile species penetrate the membrane and various transport phenomena are induced in the system²¹. Membranes in general have the ability to generate potentials when they are used to separate electrolyte solutions of different concentrations. This property is attributed to the presence of a net charge^{27,28,30-46} probably due to adsorption of anions or cations. The quantity of charge required to generate potentials, particularly when dilute solutions are used, is small. This, of course, is dependent on the porosity of the membrane. If the membrane pores are too wide well defined potentials can be obtained. But if the membrane pores are small, a little charge on it can give ideal potentials according to the Nernst equation

$$E_m = (RT / F) \ln a_1 / a_2 \quad (5.1)$$

where a_1 and a_2 are the activities of the two solutions on either side of the membrane, E_m is the membrane potential and R , T and F have their usual meanings.

The values of membrane potential E_m (mV) observed across lead tungstate membrane are positive when the membrane is used to separate dilute solutions (dilute solution side taken as positive). The values are low when the membrane is used to separate concentrated solution of an electrolyte whereas it increases as the solutions are diluted and reach to a maximum value. This means the parchment supported membrane is negatively charged (cation selective) and selectivity increases with dilution. The negative charge may be attributed to the preferential adsorption of hydroxyl ions from water and / or nitrate ions present in the solution used for the preparation of the membrane.

Two important factors which control electrolyte permeability through a membrane are charge on the membrane and its porosity. Parchment paper, except for the presence of some stray and end carboxylic group, contains very few fixed groups. Deposition of inorganic precipitate gives rise to a net negative charge on membrane surface in the dilute solutions of a 1:1 electrolyte leading to the type of ionic distribution associated with the electrical double layer²⁹. The stepwise change in membrane potential or the selectivity character of the membrane electrolyte system may readily be explained in terms of the structural change produced in the electrical double layer at the interfaces.

In hen egg shell membrane the commonest substance which forms the membrane is Keratin. Though this protein seems to take many forms and to have exactly the same properties in different solutions⁴⁷⁻⁵⁰. According to Kitchava et al.⁵¹ the outer layer of the egg vitelline membrane consist of polypeptides showing mostly α - helix structure, whereas the inner layer mainly contains peptides with randomcoil structure. Very little is known about the relative proportions of yolk, white and the shell membrane in the egg of lower animals, although the minerological and morphological structure of shell is well understood⁴⁹.

An interesting point with the values of E_m is the fact that these are negative in all the electrolyte concentration ranges. However, the value of E_m decreases algebraically as the electrolyte concentration across the membrane is increased. This means that the membrane in contact with dilute electrolyte solutions is anion selective whereas the anion selectivity decreases as the concentration across the membrane is increased. The egg shell membrane is considered to be negatively charged in contact with water. It is quite probable that in these cases the negative charge is due to the film attachment of hydroxide ions from water and few inorganic groups of organic fibers⁵⁰ constituting the egg shell membrane. An equivalent number of protons and/or cations, some closely held in the fixed part of the double layer and the remainder in the diffused portion, is left in the solution. By the addition of uni-valent electrolytes, there will be a tendency for cations to accumulate on the solution side of the fixed double layer by increasing the positive charge density, the interfacial potential difference changed thereby changing the overall membrane potential and the membrane becomes less selective. If the electrolyte concentrations are further increased the overall membrane potential or the selectivity character of the membrane changes.

The fixed groups present in well characterized ionexchange membrane can be easily estimated by titration. This procedure was used by Sollner⁵² to estimate the end groups and stray carboxylic groups present in the collodion material. Lakshminarayanaiah⁵³ in his studies with thin membranes of parlodion, used two methods the isotopic and the potentiometric to evaluate the apparent fixed charge on the membrane material. In the present studies the titration method proved inconvenient and very inaccurate, while the isotopic method was described in view of the strong ionic adsorption phenomena

exhibited by these systems. Consequently the potentiometric method based on fixed charge theory of membrane potential has been used for the evaluation of effective fixed charge density of lead tungstate parchment supported membrane and hen egg shell biological membrane.

Fixed Charge Theory of Teorell - Meyer - Sievers (TMS) :

The fixed charge concept of Teorell^{2,3}, Meyer and Sievers⁴ for charged membranes is a pertinent starting point for the investigation of the actual mechanisms of the ionic or molecular processes which occur in the membrane phase. According to this theory membrane potential is considered to be composed of two Donnan potential at the two solution- membrane interfaces and a diffusion potential arising from unequal concentration of the two membrane phases. These authors derived following equation for membrane potential in millivolts at 25°C applicable to a highly idealized system, viz:

$$E_m = 59.2 \left[\log \frac{C_2 \left(\sqrt{4C_1^2 + \bar{X}^2 + \bar{X}} \right)}{C_1 \left(\sqrt{4C_2^2 + \bar{X}^2 + \bar{X}} \right)} + \bar{U} \log \frac{\sqrt{4C_2^2 + \bar{X}^2 + \bar{X}} \bar{U}}{\sqrt{4C_1^2 + \bar{X}^2 + \bar{X}} \bar{U}} \right] \quad (5.2)$$

where $\bar{U} = (\bar{u} - \bar{v}) / (\bar{u} + \bar{v})$, \bar{u} and \bar{v} are the mobilities of cation and anion respectively in the membrane phase; \bar{X} is the charge on the membrane expressed in equivalents/litre of imbibed solution. Equation (5.2) has been frequently used for the evaluation of the fixed charge density \bar{X} of a membrane²⁹. In order to evaluate this parameter for the simple case of 1:1 electrolyte and membrane carrying a net charge of unity ($\bar{X} = \pm 1$), theoretical concentration potentials E_m existing across the membrane were calculated as a function of $\log C_2$, are given in Table 5.3 - 5.4. The ratio (C_2/C_1) being kept at

constant value of 10 for different mobility ratios, \bar{u}/\bar{v} and plotted as shown in Figs. (5.3-5.4). The observed membrane potential values using various 1:1 electrolyte are plotted in the same graph as a function of $\log 1/C_2$. The experimental curve is shifted horizontally until it coincides with one of the theoretical curves. The extent of this shift gives $\log \bar{X}$ and the coinciding theoretical curves gave the value for \bar{u}/\bar{v} in Figs. (5.3-5.4). The observed membrane potential values for lead tungstate parchment supported membrane were plotted in the Fig. (5.3), while for hen egg shell membrane these are plotted in Fig. (5.4).

Table 5.3

Theoretical values of membrane potential E_m (mV) calculated from Teorell- Meyer - Sievers method for different mobility ratio (\bar{u}/\bar{v}) for $\bar{X} = 1$ at different concentrations.

Concentration (Mol/l) C_2/C_1	Mobility ratio (\bar{u}/\bar{v})					
	0.2	0.4	0.6	0.8	1.0	1.2
1.0/0.1	15.1	30.0	45.3	46.0	45.0	34.0
0.5/0.05	35.0	40.0	47.6	47.0	50.2	50.0
0.1/0.01	50.0	50.1	50.0	55.2	55.2	55.3
0.05/0.005	56.0	56.5	56.0	58.0	59.0	59.0
0.01/0.001	59.0	59.0	59.1	59.0	59.9	59.9
0.005/0.0005	60.0	60.1	60.1	60.2	60.2	60.3
0.001/0.0001	60.1	60.0	60.2	60.1	60.2	60.2

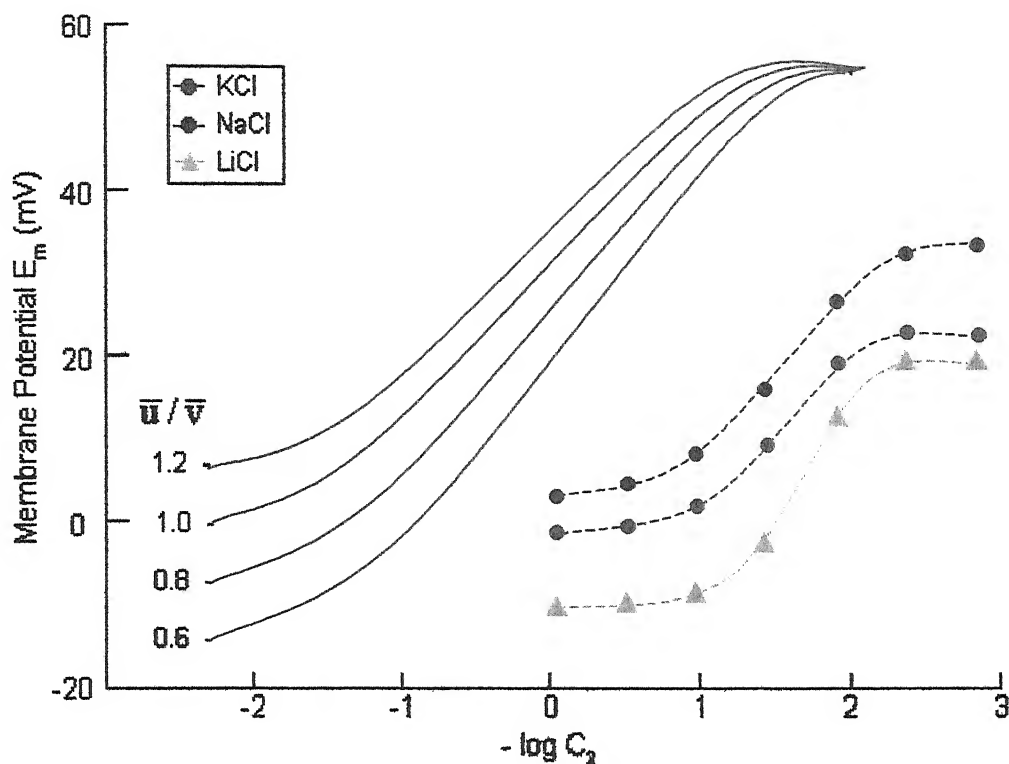


Fig. 5.3

Plots of membrane potentials E_m Vs $-\log C_2$ smooth curve on the left are the theoretical potential at $\bar{X}=1$ and for the different mobility ratio \bar{u}/\bar{v} . The broken curves on the right are the observed membrane potentials for lead tungstate membrane in contact with various 1:1 electrolytes.

Table 5.4

Theoretical values of membrane potential E_M (mV) calculated from Teorell-Meyer - Sievers method for different mobility ratio (\bar{u}/\bar{v}) for $\bar{X} = -1$ at different concentrations.

Concentration (Mol/l) C_2/C_1	Mobility ratio (\bar{u}/\bar{v})					
	0.4	0.5	0.6	0.7	0.8	0.9
1.0/0.1	-9.2	-12.4	-16.3	-18.6	-21.2	-23.2
0.5/0.05	-11.6	-15.3	-18.8	-20.3	-23.0	-25.3
0.1/0.01	-15.7	-18.1	-21.10	-23.5	-26.4	-28.5
0.05/0.005	-22.8	-22.9	-25.4	-27.7	-30.1	-32.3
0.01/0.001	-30.0	-32.6	-35.0	-37.0	-38.3	-38.2
0.005/0.0005	-37.1	-43.2	-46.3	-47.2	-48.2	-47.8
0.001/0.0001	-54.10	-54.10	-54.10	-54.3	-54.5	-54.4

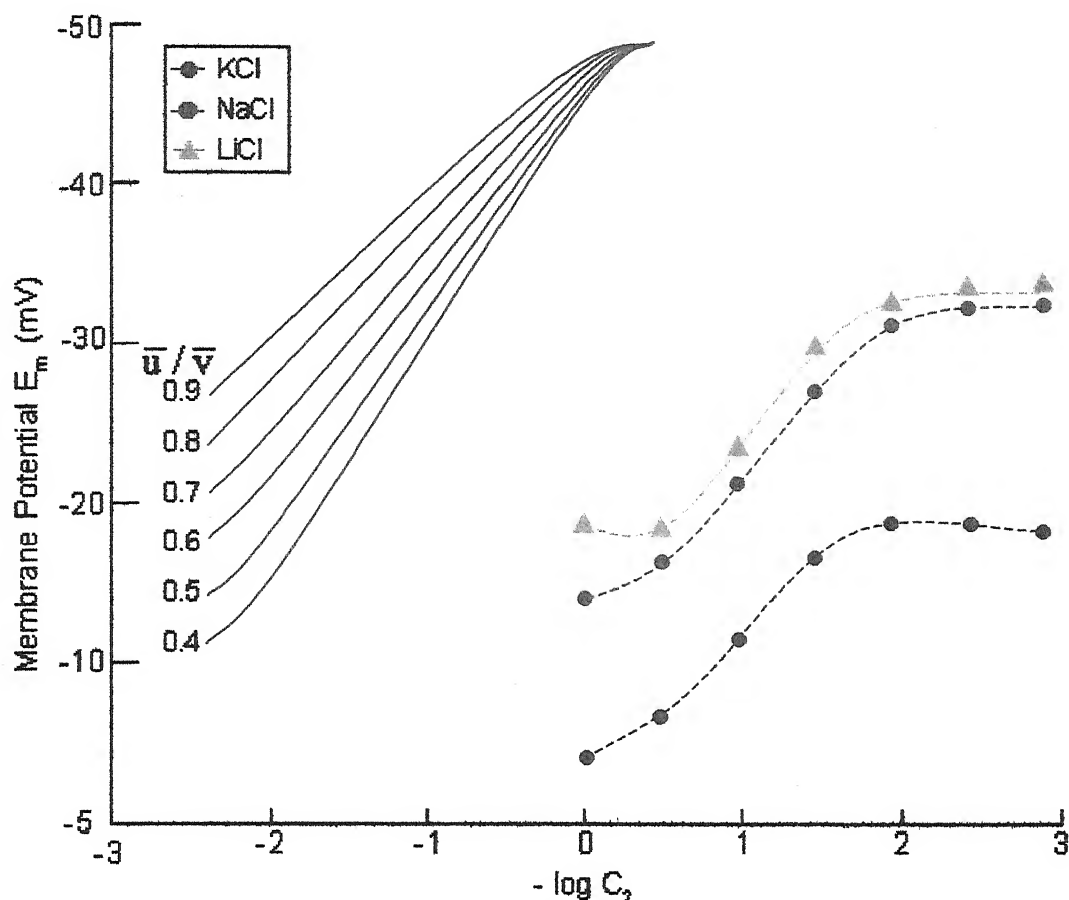


Fig. 5.4

Plots of membrane potentials E_m Vs $-\log C_2$ smooth curve on the left are the theoretical potential at $\bar{X}=-1$ and for the different mobility ratio \bar{u}/\bar{v} . The broken curves on the right are the observed membrane potentials for hen egg shell membrane in contact with various 1:1 electrolytes.

The values of \bar{X} and \bar{u}/\bar{v} derived in this way for two membranes with various 1:1 electrolytes combinations are given in Table 5.5. It is, however, noted that the experimental curves for hen egg shell membrane after shifting horizontally did not overlap completely with any of the horizontal curves in all the electrolyte concentration ranges studies. This discrepancy is not peculiar for lead tungstate membrane as well as for other systems^{31-33, 54-57}. Hen egg shell membrane has the similar nature of observed membrane potential as the potential measured across duramater, the membrane surrounding the brain of buffalo⁵⁸ and

the peritoneal membrane⁵⁹, goat erythrocytes⁶⁰, plasma fibronectin of buffalo⁶¹ (*Babulis babulis*), and rabbit articular chondrocytes⁶².

Table 5.5

Value of effective fixed charge density \bar{X} (eq/l) and mobility ratio (\bar{u}/\bar{v}) for various membrane electrolyte systems using Teorell-Meyer-Sievers method at $25 \pm 0.1^\circ\text{C}$.

Membranes	Parameters	Electrolyte		
		KCl	NaCl	LiCl
Lead tungstate	$(\bar{X}) \times 10^2$	3.6	1.5	4.6
	(\bar{u}/\bar{v})	1.0	0.8	0.6
Hen egg shell	$(\bar{X}) \times 10^2$	2.6	4.10	4.7
	(\bar{u}/\bar{v})	0.9	0.7	0.5

Altug and Hair Theory :

Altug and Hair¹⁵ have given an ingenious and indirect method which has been developed on the lines of Teorell's model^{2,3} for the evaluation of membrane fixed charge density $\omega\bar{X}$ where \bar{X} represents the number of ionized sites per unit volume and $\omega = \pm 1$ for positive or negative membranes. According to the Teorell's model, the behaviour for a charged membrane in an electrolyte solution can be characterized in terms of ionic mobilities, concentrations and fixed charge in the membrane.

In a modification of this type plotting Altug and Hair¹⁵ evaluated \bar{X} for glass membrane, choosing solution values for \bar{u} and \bar{v} . In this procedure, a value for \bar{X} was assumed and r_1 and r_2 , the distribution ratios, were calculated according to eqs. (5.3-5.5) for the given electrolyte concentrations C_1 and C_2 .

$$\pi_1 = -\frac{RT}{F} \ln r_1 \quad (5.3)$$

$$\pi_2 = -\frac{RT}{F} \ln r_2 \quad (5.4)$$

$$r = \left[1 + \left(\frac{w\bar{X}}{2a} \right)^2 \right]^{1/2} - \left(\frac{w\bar{X}}{2a} \right) \quad (5.5)$$

The theoretical membrane potential was then determined from eqn. (5.6) for 1.0 to 1.0×10^{-4} Mol/l concentration range.

$$E_{cal} = \left(\frac{u-v}{u+v} \right) \left(\frac{RT}{F} \right) \ln \left[\frac{a_1(r_1 u + v/r_1)}{a_2(r_2 u + v/r_2)} \right] + \frac{RT}{F} \ln \frac{r_2}{r_1} \quad (5.6)$$

The values of Donnan potential ($\pi_1 + \pi_2$), the diffusion potential ($\phi_2 - \phi_1$) and the total membrane potential E_{cal} for various concentration of KCl (for different values of \bar{X} varying for 0.4 N to 0.006 N) are given in Tables (5.6-5.10). By following the algebraic procedure, a series of theoretical curves were obtained for different \bar{X} values with KCl electrolyte and are shown by solid lines in Figs. (5.5 - 5.6). At the same time curves were also plotted in same Figs. (5.5-5.6) between the experimentally determined membrane potential values for KCl electrolyte in the same concentration range for both the membranes.

Table 5.6

Calculated values of Donnan potentials (π_1 and π_2), diffusion potentials ($\phi_2 - \phi_1$) and total membrane potentials $E_{cal} = (\pi_1 + \pi_2) + (\phi_2 - \phi_1)$ for membrane fixed ion concentrations $\bar{X} = -0.006$ and -0.008 with various concentration of KCl

$\frac{\bar{X}}{N}$	Concentration C_2 / C_1 (Mol/l)	$(\pi_1 + \pi_2)$ (mV)	$(\phi_2 - \phi_1)$ (mV)	E_{cal} (mV)
-0.006	1.0 / 0.1	0.65	-1.11	-0.46
	0.5 / 0.05	1.33	-1.10	0.23
	0.1 / 0.001	6.70	-1.09	5.62
	0.05 / 0.005	12.84	-1.02	11.82
	0.1 / 0.01	38.41	-0.56	37.85
	0.005 / 0.0005	48.50	-0.26	48.24
	0.001 / 0.0001	57.22	-0.03	57.19
-0.008	1.0 / 0.1	0.87	-1.11	-0.23
	0.5 / 0.05	1.82	-1.13	-0.69
	0.1 / 0.01	8.85	-1.06	7.79
	0.05 / 0.005	16.48	-0.98	15.50
	0.1 / 0.001	43.03	-0.47	42.56
	0.005 / 0.0005	51.67	-0.36	51.31
	0.001 / 0.0001	57.72	-0.01	57.71

Table 5.7

Calculated values of Donnan potentials (π_1 and π_2), diffusion potentials ($\phi_2 - \phi_1$) and total membrane potentials $E_{cal} = (\pi_1 + \pi_2) + (\phi_2 - \phi_1)$ for membrane fixed ion concentrations $\bar{X} = -0.01$ and -0.02 with various concentration of KCl

$\frac{\bar{X}}{N}$	Concentration C_2 / C_1 (Mol/l)	$(\pi_1 + \pi_2)$ (mV)	$(\phi_2 - \phi_1)$ (mV)	E_{cal} (mV)
-0.01	1.0 / 0.1	1.13	-1.27	-0.14
	0.5 / 0.05	2.25	-1.11	1.14
	0.1 / 0.001	10.88	-1.08	9.81
	0.05 / 0.005	19.69	-0.96	18.93
	0.1 / 0.01	46.26	-0.39	45.87
	0.005 / 0.0005	53.37	0.01	53.36
	0.001 / 0.0001	57.84	0.01	57.39
-0.02	1.0 / 0.1	2.26	-1.13	1.13
	0.5 / 0.05	4.28	-1.07	3.22
	0.1 / 0.01	19.72	0.97	18.74
	0.05 / 0.005	31.21	-0.76	30.44
	0.1 / 0.001	53.21	-0.18	53.02
	0.005 / 0.0005	56.68	-0.09	56.59
	0.001 / 0.0001	58.22	0.01	58.19

Table 5.8

Calculated values of Donnan potentials (π_1 and π_2), diffusion potentials ($\phi_2 - \phi_1$) and total membrane potentials $E_{cal} = (\pi_1 + \pi_2) + (\phi_2 - \phi_1)$ for membrane fixed ion concentrations $\bar{X} = -0.03$ and -0.04 with various concentration of KCl

$\frac{\bar{X}}{N}$	Concentration C_2 / C_1 (Mol/l)	$(\pi_1 + \pi_2)$ (mV)	$(\phi_2 - \phi_1)$ (mV)	E_{cal} (mV)
-0.03	1.0 / 0.1	4.43	-1.12	3.31
	0.5 / 0.05	6.92	-0.91	6.01
	0.1 / 0.001	25.41	-0.84	24.20
	0.05 / 0.005	38.40	-0.58	37.82
	0.1 / 0.01	57.06	-0.08	56.98
	0.005 / 0.0005	58.03	0.01	58.02
	0.001 / 0.0001	58.21	0.01	58.12
-0.04	1.0 / 0.1	4.08	-1.08	3.0
	0.5 / 0.05	7.01	-0.90	6.11
	0.1 / 0.01	31.45	-0.74	30.71
	0.05 / 0.005	43.08	-0.46	45.62
	0.1 / 0.001	57.03	-0.06	53.97
	0.005 / 0.0005	58.16	-0.01	58.15
	0.001 / 0.0001	58.21	-0.01	58.2

Table 5.9

Calculated values of Donnan potentials (π_1 and π_2), diffusion potentials ($\phi_2 - \phi_1$) and total membrane potentials $E_{cal} = (\pi_1 + \pi_2) + (\phi_2 - \phi_1)$ for membrane fixed ion concentrations $\bar{X} = -0.05$ and -0.06 with various concentration of KCl

$\frac{\bar{X}}{N}$	Concentration C_2 / C_1 (Mol/l)	$(\pi_1 + \pi_2)$ (mV)	$(\phi_2 - \phi_1)$ (mV)	E_{cal} (mV)
-0.05	1.0 / 0.1	5.59	-1.09	4.50
	0.5 / 0.05	12.11	-1.01	11.10
	0.1 / 0.001	35.39	-0.66	34.73
	0.05 / 0.005	45.98	-0.38	45.60
	0.1 / 0.01	57.01	-0.03	57.07
	0.005 / 0.0005	57.70	-0.01	57.69
	0.001 / 0.0001	58.22	-0.001	58.21
-0.06	1.0 / 0.1	6.3	-1.11	5.62
	0.5 / 0.05	12.86	-1.03	11.83
	0.1 / 0.01	38.53	-0.59	37.94
	0.05 / 0.005	48.52	-0.33	48.20
	0.1 / 0.001	55.92	-0.13	55.79
	0.005 / 0.0005	57.95	-0.01	57.94
	0.001 / 0.0001	58.22	-0.01	58.21

Table 5.10

Calculated values of Donnan potentials (π_1 and π_2), diffusion potentials ($\phi_2 - \phi_1$) and total membrane potentials $E_{cal} = (\pi_1 + \pi_2) + (\phi_2 - \phi_1)$ for membrane fixed ion concentrations $\bar{X} = -0.1$ and -0.4 with various concentration of KCl

$\frac{\bar{X}}{N}$	Concentration C_2 / C_1 (Mol/l)	$(\pi_1 + \pi_2)$ (mV)	$(\phi_2 - \phi_1)$ (mV)	E_{cal} (mV)
-0.1	1.0 / 0.1	10.90	-1.08	9.82
	0.5 / 0.05	19.75	-0.63	19.13
	0.1 / 0.001	46.22	-0.39	45.83
	0.05 / 0.005	53.33	-0.18	53.15
	0.1 / 0.01	57.86	0.01	57.85
	0.005 / 0.0005	58.06	0.01	58.05
	0.001 / 0.0001	58.22	0.01	58.21
-0.4	1.0 / 0.1	31.45	-0.75	30.70
	0.5 / 0.05	43.03	-0.52	42.51
	0.1 / 0.01	56.59	-0.06	56.53
	0.05 / 0.005	57.74	-0.03	57.71
	0.1 / 0.001	58.01	0.02	57.99
	0.005 / 0.0005	58.10	0.01	58.09
	0.001 / 0.0001	58.22	0.01	58.21

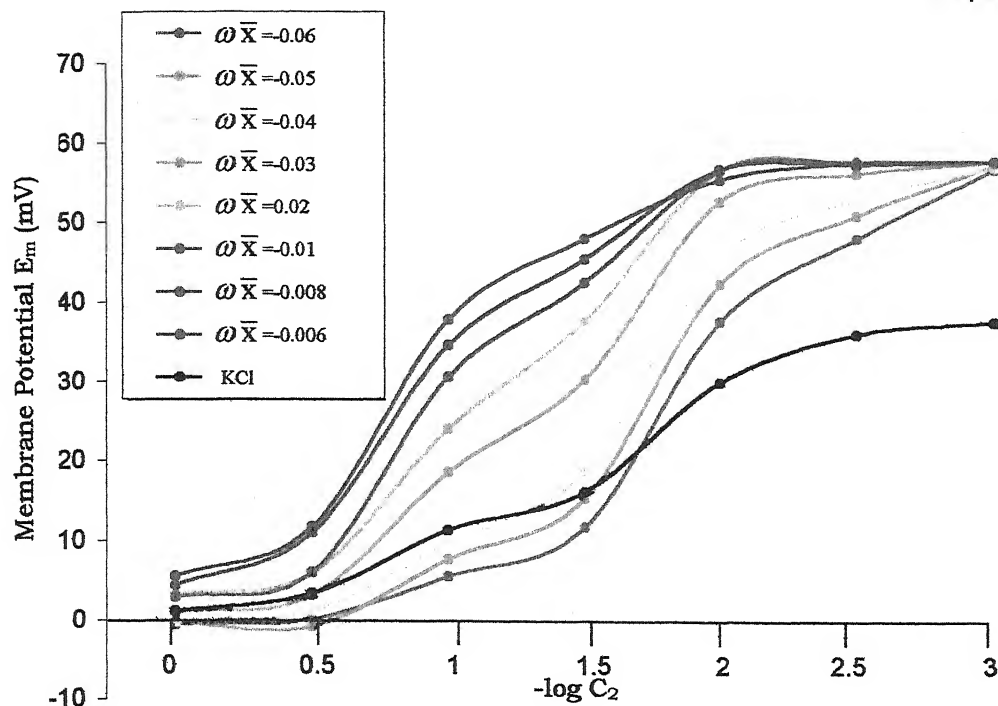


Fig. 5.5

Plots of E_m against $-\log C_2$. Smooth curves are the theoretical potentials for different charge density. The broken line curve is the observed membrane potential for parchmet supported lead tungstate membrane using KCl electrolyte.

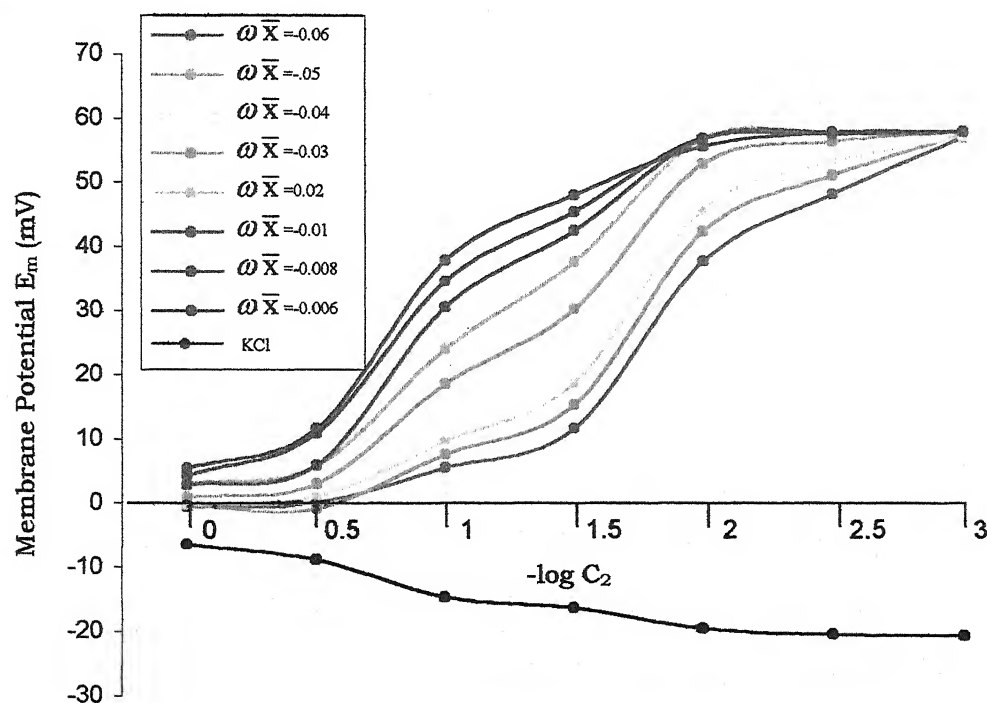


Fig. 5.6

Plots of E_m against $-\log C_2$. Smooth curves are the theoretical potentials for different charge density. The broken line curve is the observed membrane potential for hen egg shell membrane using KCl electrolyte.

The theoretical curve which coincided with the experimental curve gave the value for \bar{X} as shown in figures. In this way the value of charge density \bar{X} of any of the membrane was determined. The fixed charge density of lead tungstate and hen egg shell membranes determined by the Altug and Hair¹⁵ method were found 2.9 and 1.8 eq./l respectively for the membranes. Taking these values of the charge density the experimental and calculated value of the membrane potential for NaCl and LiCl are shown in Figs. (5.7-5.8).

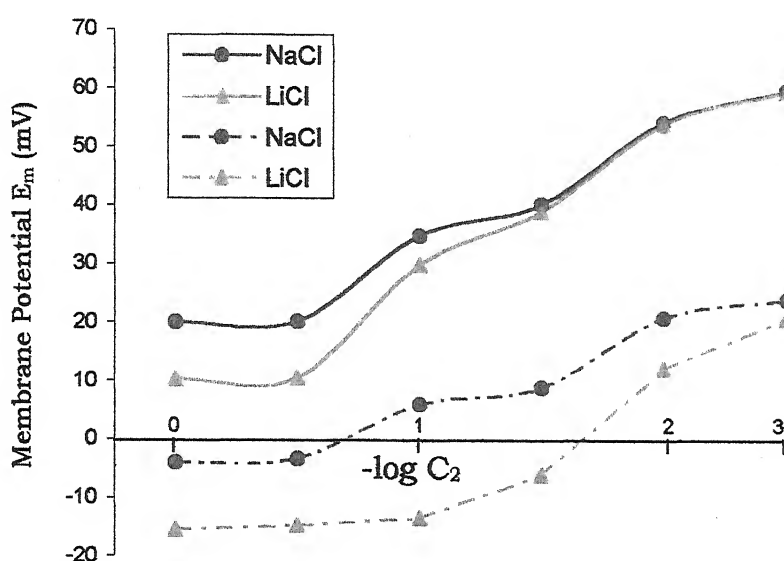


Fig. 5.7

Plots of observed and theoretically calculated membrane potentials against $-\log C_2$ across parchment supported lead tungstate membrane assuming $\omega \bar{x} = -0.02N$ for different electrolytes smooth curves show calculated values and broken show observed values.

Fair agreement with theory or theoretical curves is obtained for LiCl but not for NaCl for lead tungstate membrane and similarly for NaCl but not for LiCl for hen egg shell membrane. It should be noted that the cation and anion mobilities used in the present calculations are those of the free solution⁶³. Diffusion data in literature however, indicate that the ion mobilities go through a considerable change in a parchment supported membrane. The fair agreement

between observed and calculated values in the case of the salt solution, indicates that the membrane is behaving in a manner closely allied to that predicted by TMS²⁻⁴ and that the cation and anion mobility ratio is little affected by the membrane. In the case of LiCl solution the cation and anion mobility ratio may be altered by the membrane the mobility of the cation being decreased relative to that of anion.

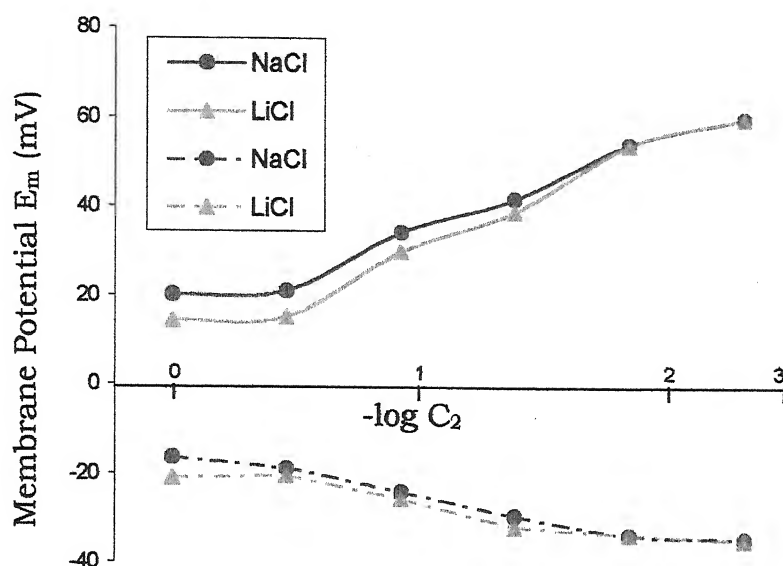


Fig. 5.8

Plots of observed and theoretically calculated membrane potentials against $-\log C_2$ across hen egg shell membrane assuming $\omega \bar{x} = -0.02N$ for different electrolytes smooth curves show calculated values and broken show observed values.

Kabatake et al. Theory :

Kabatake et al.⁶⁴ on the basis of the thermodynamics of irreversible processes derived the following equation for the electrical potential E_m which arises when a negatively charged membrane separates two solutions of an 1:1 electrolyte of different concentrations C_1 and C_2 ($C_1 < C_2$), which is also used here for the evaluation of the thermodynamically effective fixed charge density of membranes.

$$E_m = - \left(\frac{RT}{F} \right) \left[\frac{1}{\beta} \ln \frac{C_2}{C_1} - \left(1 + \frac{1}{\beta} - 2\alpha \right) \ln \left(\frac{C_2 + \alpha \beta \bar{X}}{C_1 + \alpha \beta \bar{X}} \right) \right] \quad (5.7)$$

where $\alpha = \frac{u}{u+v}$ and $\beta = 1 + \frac{KF\bar{X}}{v}$

u and v are the molar mobilities of positive and negative ions, F is Faraday constant and K is a constant dependent upon the viscosity of the solution and structural details of the polymer network of which the membrane is composed. To evaluate the membrane parameters, α , β and \bar{X} , two limiting forms of the above equation were derived.

- (a) When the external salt concentration C_2 is sufficiently small with γ fixed, eqn. (5.7) may be expanded to give :

$$|E_m^\sigma| = \left(\frac{1}{\beta}\right) \ln \gamma - \left(\frac{\gamma-1}{\alpha \beta \lambda}\right) \left(1 + \frac{1}{m} - 2\alpha\right) \left(\frac{C_2}{\bar{X}}\right) + \dots \quad (5.8)$$

where $|E_m^\sigma| = (E_m / RT)$

and $\gamma = C_2 / C_1$

- (b) When the salt concentration C_2 is high, eqn (5.7) may be written as :

$$\frac{1}{t_-} = \left(\frac{1}{1-\alpha}\right) + \left[\left(\frac{(1+\beta-2\alpha\beta)\alpha(\gamma-1)\alpha}{2(1-\alpha)^2 \ln \gamma}\right)\right] \left(\frac{\bar{X}}{C_2}\right) + \dots \quad (5.9)$$

Where t_- is the apparent transference number of coions (anions) in a negatively charged membrane defined by

$$|E_m^\sigma| = (1 - 2t_-) \ln \gamma \quad (5.10)$$

The values of t_- calculated from observed membrane potentials using eqn. (5.10) for lead tungstate parchment supported membrane and hen egg shell biological membrane are given in Tables 5.11-5.12. Eqn. (5.8) was used to give the value of β (Table 5.13) and a relation between α and \bar{X} by evaluating the intercept and the initial slope of the plot of $|E_m^\sigma|$ against C_2 (Figs 5.9 - 5.10), while eqn. (5.10) was used to evaluate α (Table 5.13) from the intercept of a plot $1/t_-$ against $1/C_2$ (Figs. 5.11 - 5.12). The values of \bar{X} were determined by inserting this value of α in the relation between α and \bar{X} obtained earlier.

Table 5.11

Transference number t_- of coions (Anions) derived from observed membrane potential at various electrolyte concentrations through parchment supported lead tungstate membrane.

Concentration (Mol/l) C_2 / C_1	Electrolyte		
	KCl	NaCl	LiCl
1.0/0.1	0.49	0.54	0.64
0.5/0.05	0.48	0.52	0.63
0.1/0.01	0.41	0.45	0.61
0.05/0.005	0.36	0.42	0.56
0.01/0.001	0.26	0.38	0.35
0.005/0.0005	0.21	0.32	0.33
0.001/0.0001	0.20	0.30	0.32

Table 5.12

Transference number t_- of coions (anions) derived from observed membrane potential at various electrolyte concentrations through hen egg shell membrane..

Concentration (Mol/l) C_2 / C_1	Electrolyte		
	KCl	NaCl	LiCl
1.0/0.1	0.46	0.37	0.34
0.5/0.05	0.44	0.35	0.32
0.1/0.01	0.38	0.31	0.29
0.05/0.005	0.36	0.26	0.24
0.01/0.001	0.34	0.23	0.22
0.005/0.0005	0.32	0.22	0.20
0.001/0.0001	0.30	0.21	0.18

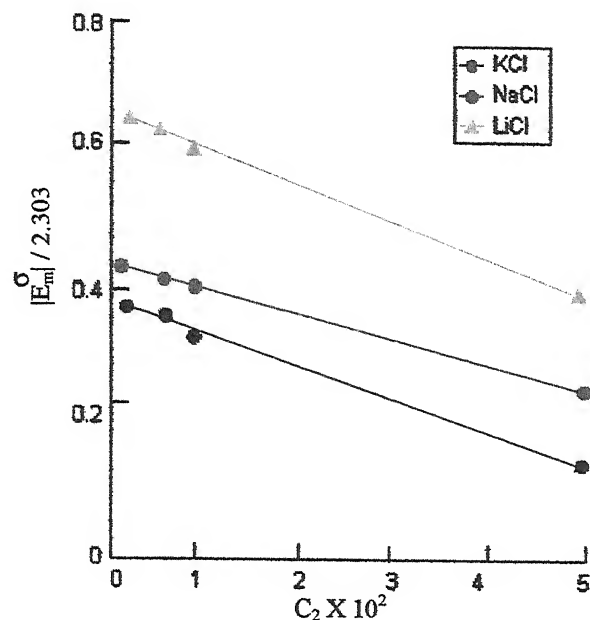


Fig. 5.9

Plots of $|E_m^\sigma| / 2.303$ against $C_2 \times 10^2$ for lead tungstate membrane in contact with various 1:1 electrolyte solutions.

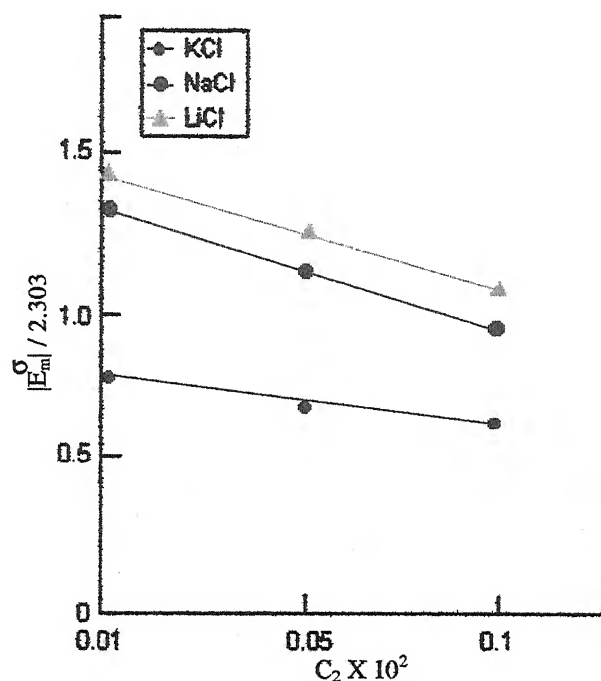


Fig. 5.10

Plots of $|E_m^\sigma| / 2.303$ against $C_2 \times 10^2$ for hen egg shell membrane in contact with various 1:1 electrolyte solutions.

Table 5.13

Values of the membrane parameters α and β for various membrane electrolytes systems at $\gamma=10$.

Electrolyte	KCl		NaCl		LiCl	
Membrane	α	β	α	β	α	β
Lead tungstate	0.52	1.6	0.45	2.4	0.39	2.7
Hen egg shell	0.59	3.1	0.64	1.8	0.68	1.7

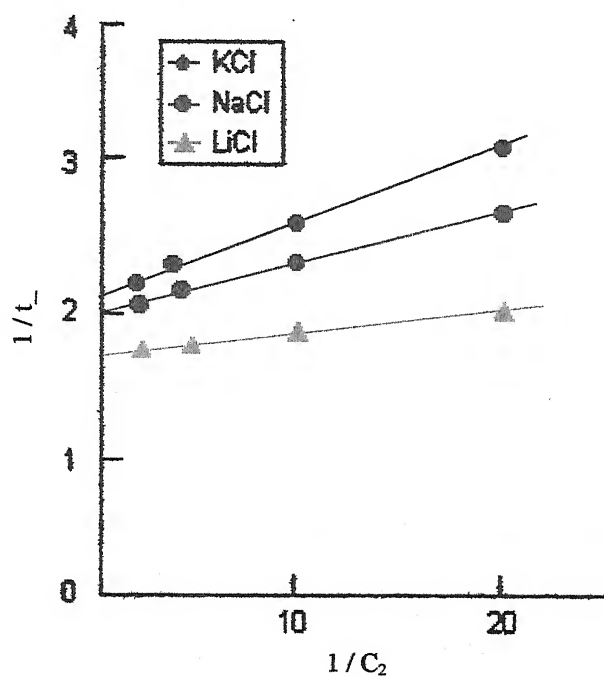


Fig. 5.11

Plot of $1/t_-$ against $1/C_2$ for lead tungstate membrane using 1:1 electrolyte solutions at constant γ ($\gamma = 10$)

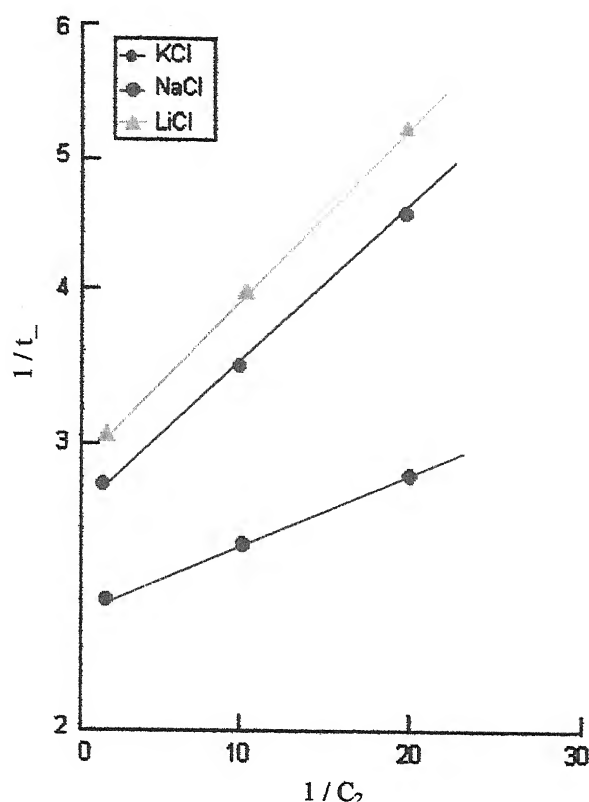


Fig. 5.12

Ploto of $1/t_-$ against $1/C_2$ for hen egg shell membrane using 1:1 electrolyte solutions at constant γ ($\gamma = 10$)

Confirmation of Kobatake's Equation on Model and Biological Membranes :

Once the values of the parameters α , β and \bar{X} for a given membrane-electrolyte system have been determined one can get the theoretical E_m using eqn. (5.7) and compare it with the corresponding experimental data. For this comparison eqn. (5.7) can be rewritten in the following form as suggested by Kobatake and co-workers⁶⁴.

$$\frac{\gamma - e^q}{e^q - 1} = Z \quad (5.11)$$

with q and Z defined by

$$q = |E_m^\sigma| + \frac{(1-2\alpha) \ln \gamma}{(1/\beta) + (1-2\alpha)}$$

$$\text{and } Z = C_2/\alpha\beta \bar{X}.$$

Thus if eqn. (5.11) is valid, the value of $(\gamma - e^q)/(e^q - 1)$ calculated from the measured E_m with predetermined α , β and \bar{X} and the given value of γ must fall on a straight line which has a unit slope and passes the co-ordinate origin when plotted against Z . This behaviour should be observed irrespective of the value of γ and the kind of membrane - electrolyte system used. Figs. (5.13-5.14) demonstrate that the theoretical prediction of eqn. (5.11) or eqn. (5.7) is borne out quite satisfactory by my experimental results on parchment supported lead tungstate membrane and hen egg shell membrane respectively.

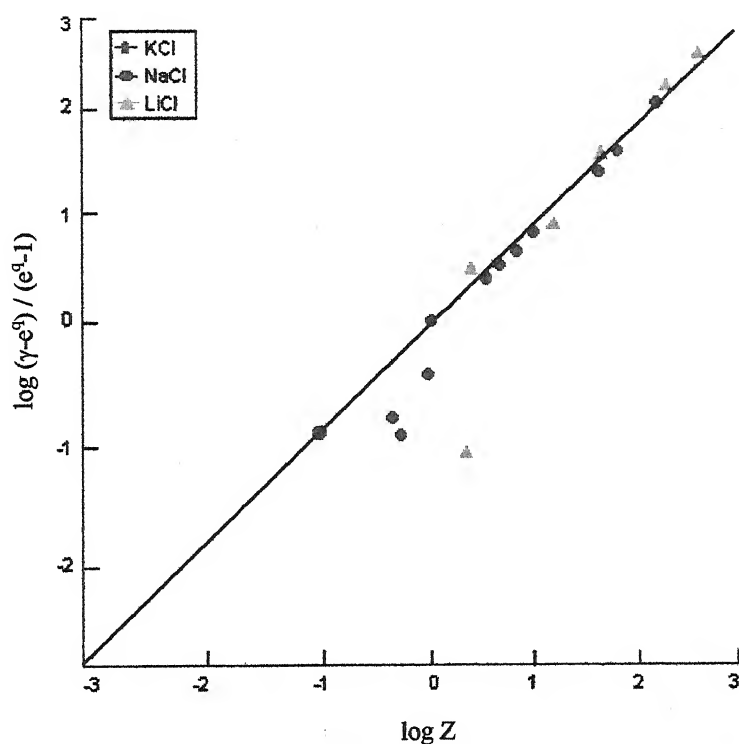


Fig. 5.13

Plots of $\log (\gamma - e^q) / (e^q - 1)$ against $\log Z$ for lead tungstate membrane in contact with various 1:1 electrolytes.

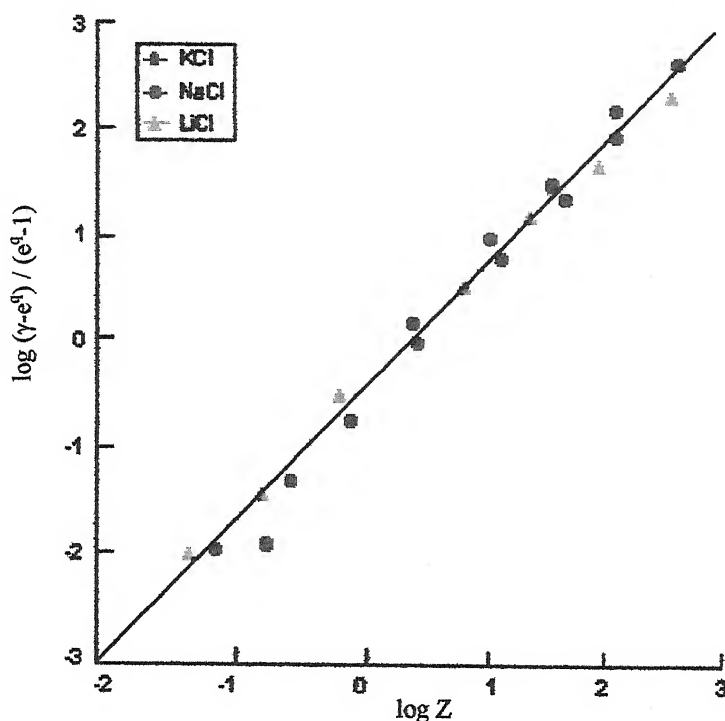


Fig. 5.14

Plots of $\log (\gamma e^q) / (e^q - 1)$ against $\log Z$ for hen egg shell membrane in contact with various 1:1 electrolytes.

Nagasawa Method for Membrane Charge Density :

Nagasawa et. al.²⁵ derived an equation for the membrane potential existing across a charge membrane. The total membrane potential E_m was considered as the sum of a diffusion potential E_d inside the membrane and the electrostatic potential differences E_e between the membrane surfaces and the electrolyte solutions on both sides of the membrane. The diffusion potential E_d was obtained by integrating the basic flow equation for diffusion⁶⁵ while the electrostatic potential differences was calculated from the Donnan's theory^{66,67} stated mathematically.

$$E_m = E_d + E_e \quad (5.12 \text{ a})$$

$$\text{where } -E_d = \int_1^2 \frac{J_o}{F \bar{C}_0} \frac{\phi X}{(\bar{C}_- + \phi X) u \bar{C}_- v} dx + \frac{RT}{F} \int_1^2 \frac{(\bar{C}_- + \phi X) u}{(\bar{C}_- + \phi X) u + \bar{C}_- v} d \ln \bar{a}_+$$

$$- \frac{RT}{F} \int_1^2 \frac{\bar{C}_v}{(\bar{C}_- + \phi X) u + \bar{C}_- v} d \ln \bar{a}_- \quad (5.12 \text{ b})$$

$$\text{and } -E_e = -(RT/F) \ln \left(\frac{\bar{a}_1 a_2}{a_1 \bar{a}_2} \right) \quad (5.12 \text{ c})$$

where a_1 and a_2 are the activities of the electrolytes on the two sides of the membrane, the overbar refers to the phenomena in the membrane phase. J_0 is the flow of electrolyte in the absence of an external electric field, the other symbols have their usual significance. On integrating eqn. (5.12a) in the limit of high electrolyte concentrations across the membrane potential :

$$\begin{aligned} -E_m = & \frac{RT}{F} \left(\frac{\gamma-1}{\gamma} \right) \left(\frac{\phi X}{2} \right) \frac{1}{C_2} + \frac{RT}{F} \left(\frac{u-v}{u+v} \right) \frac{\left(1 - \frac{\phi X J_0}{RT \bar{C}_0 (u-v) K} \right)}{\left(1 - \frac{\phi X J_0}{2RT \bar{C}_0 v K} \right)} \ln \gamma + \\ & \frac{RT \phi X}{2Fuv} \left(\frac{J_0}{RT \bar{C}_0 K} \right)^2 \frac{\left(1 - \frac{\phi X J_0 (u+v)}{4RT \bar{C}_0 uv K} \right)}{\left(1 - \frac{\phi X J_0}{2RT \bar{C}_0 v K} \right)^2} (\gamma-1) C_2 \end{aligned} \quad (5.13)$$

At high electrolyte concentrations, eq. (5.13) can be approximated by

$$-E_m = \frac{RT}{F} \left(\frac{\gamma-1}{\gamma} \right) \left(\frac{\phi X}{2} \right) \frac{1}{C_2} + \dots \quad (5.14)$$

Equation (5.14) predicts a linear relationship between E_m and $1/C_2$ from which ϕX can be represented. Plots of $E_m / (\gamma-1) / \gamma$ versus $1/C_2$ for the membranes are represented in Figs. (5.15 - 5.16). A set of straight lines in agreement with eqn. (5.14) are obtained. The values of ϕX derived from the slope of the lines are given in Table. 5.14.

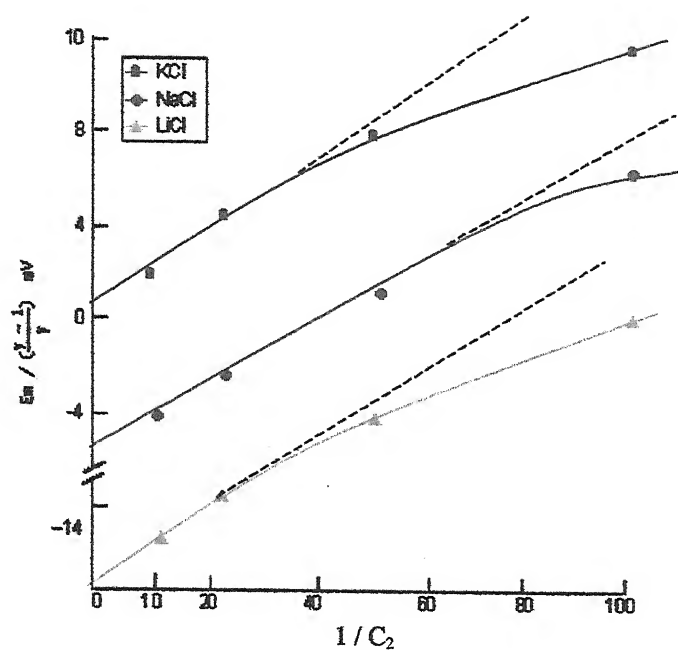


Fig. 5.15

Plots of membrane potentials $E_m / (\gamma - 1/\gamma)$ against $1 / C_2$ for lead tungstate membrane in contact with various 1:1 electrolytes.

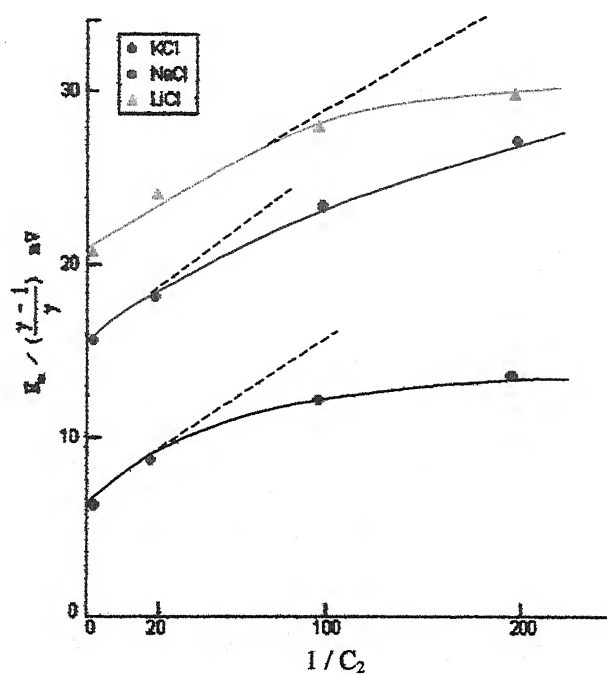


Fig. 5.16

Plots of membrane potentials $E_m / (\gamma - 1/\gamma)$ against $1 / C_2$ for hen egg shell membrane in contact with various 1:1 electrolytes.

The values of fixed charge densities evaluated from the two developed theories of Kobatake et al. and Tasaka et al. are closer to those derived from the TMS theory-the theory most widely used to interpret data on biological systems. (Table 5.14). The values obtained for parchment supported lead tungstate membrane and hen egg shell membrane vary significantly, depending on the different methods used. It is thus concluded that values of effective fixed charge densities evaluated using the different theories characterize the membranes accurately.

Table 5.14

Values of effected fixed charge densities of parchment supported lead tungstate and hen egg shell membranes using various 1:1 electrolytes derived from different theories.

Membrane	Lead tungstate			Hen egg shell		
Electrolyte	KCl	NaCl	LiCl	KCl	NaCl	LiCl
TMS Theory						
$(\bar{X}) \times 10^2 (eq/l)$	3.6	1.7	4.6	2.6	4.10	4.7
Equation (5.2)						
Kobatake et. al.						
Theory						
$(\bar{X}) \times 10^2 (eq/l)$	4.4	1.6	3.1	3.6	6.3	6.2
Equation (5.8)						
Nagosawa et. al.						
Theory						
$(\bar{X}) \times 10^2 (eq/l)$	1.9	0.98	1.9	3.8	5.2	5.4
Equation (5.14)						

Aizawa Method :

The Aizawa method is an extended form of Nagasawa et al. approaches for the evaluation of fixed charge density based on thermodynamics of irreversible processes

According Aizawa the transmembrane potential across a charged membrane has also been approximated as

$$\left(\frac{F}{RT}\right)E_m = -\ln\gamma + \ln \frac{-\phi X + \sqrt{(\phi X)^2 + 4C_2^2}}{-\phi X + \sqrt{(\phi X)^2 + 4C_1^2}} + (2t_- - 1) \ln \frac{(1-2t_-)\phi X + \sqrt{(\phi X)^2 + 4C_2^2}}{(1-2t_-)\phi X + \sqrt{(\phi X)^2 + 4C_1^2}} \quad (5.15)$$

where t_- is the transference number of anion. For a slightly charged membrane, i.e. when $\phi X \ll C$, eq. 5.15 reduces to 5.16

$$\left(\frac{F}{RT}\right)E_m = (2t_- - 1) \ln\gamma + \left(\frac{2(\gamma-1)}{\gamma}\right)t_- (1-t_-) \left(\frac{\phi X}{C_2}\right) \quad (5.16)$$

which predicts a straight line plot of $(F/RT) E_m$ against $1/C_2$ at fixed γ and allows the evaluation of t_- and ϕX from the intercept and slope of linear plot Fig. (5.17-5.18) The values of ϕX , evaluated with the help of Figs 5.17 and 5.18 using eqn. (5.16) for the parchment supported lead tungstate and hen egg shell membranes are given in Tables 5.5.

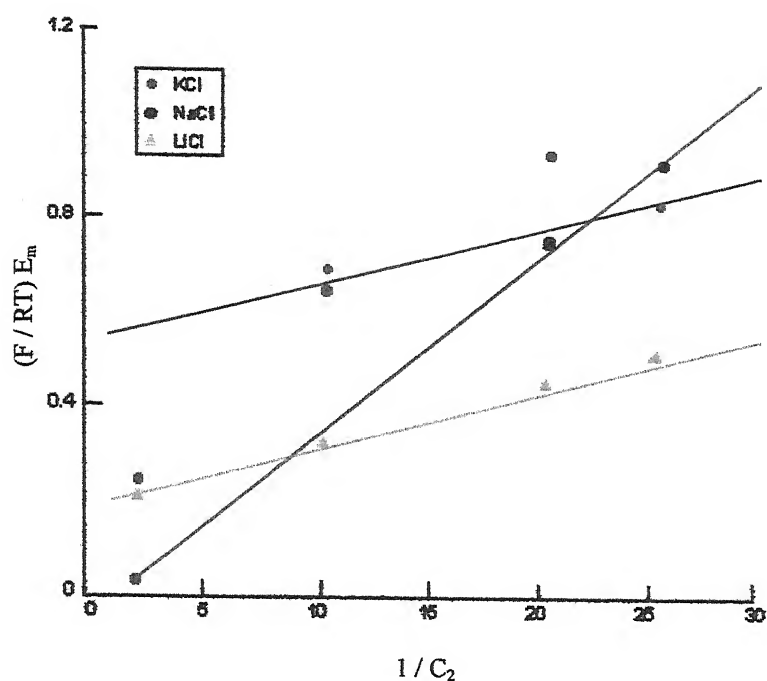


Fig. 5.17

Plots of $(F/RT)E_m$ Against $1/C_2$ for lead tungstate membrane using various 1:1 electrolytes.

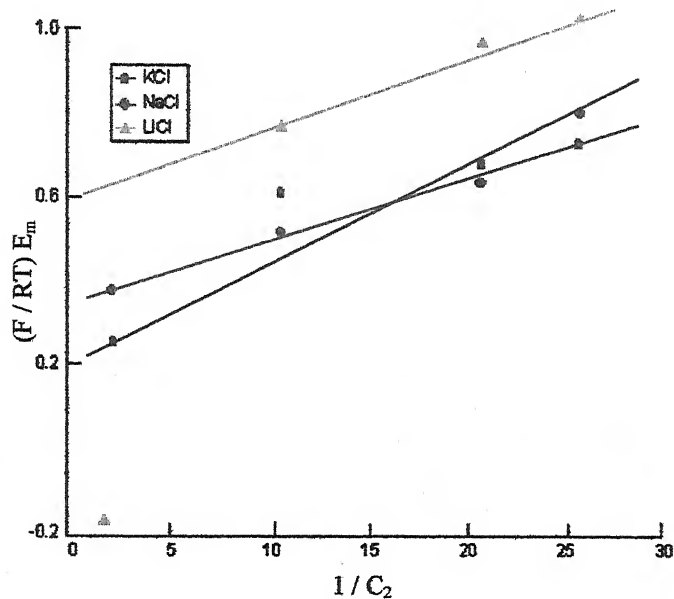


Fig. 5.18

Plots of $(F/RT)E_m$ Against $1/C_2$ for hen egg shell membrane using various 1:1 electrolytes.

Table - 5.15

Values of thermodynamically effective fixed charge density $\phi X 10^2$ (eq. /l) obtained from Aizawa's method for various membrane electrolyte systems at $25 \pm 0.1^\circ\text{C}$

Electrolytes	Membranes	
	Lead tungstate	Hen egg shell
KCl	3.9	2.8
NaCl	1.8	4.12
LiCl	4.9	4.9

Conclusion

The parchment supported inorganic precipitate lead tungstate and hen egg shell biological membranes were used for the measurement of electrical potential developed across them by using the aqueous solutions of 1:1 electrolytes. The evaluation of effective fixed charge density values of these membranes was carried out using the various well established theories of Teorell-Meyer-Sievers (TMS), Altug and Hair, Kobatake et al., Nagasawa et al. and Aizawa et al. based on the principles of irreversible thermodynamics.

The conclusions which can be drawn about the relative strengths and weaknesses of each of the theories as applied to parchment supported and biological membranes can be summarized as follows. The important point emerging from the application of TMS theory is that the mobility ratio goes through a change considerable in some cases in the membrane phase. Usually in the case of cation selective membrane (values of \bar{X} high) $(\bar{u}/\bar{v}) \rightarrow 0$ in dilute solutions and only when the membrane is in equilibrium with concentrated solutions does

$(\bar{u}/\bar{v}) \rightarrow (u/v)_{\text{solution}}$. In view of this, the approach of TMS is unreliable to evaluate charge density \bar{X} for ion-exchange membranes which have a high concentration of fixed groups. It is not that unreliable for a membrane which has a low concentration of

\bar{X} as found in this study due to the fact that the change in the values of the factor (\bar{u}/\bar{v}) is not drastic as it is with membranes of high charge density. The limitations of this conceptually useful theory which has stimulated both theoretical and experimental work, are applicable only to idealized system and this should be borne in mind when it is applied to analyze membrane phenomena.

Altug and Hair method is principally based on Teorell's model. This alternative method of plotting the membrane potential data may be expected to give \bar{X} values different from those given by TMS method. It is not very realistic to use the solution mobility values for the ratio u/v in the calculations, it is believed that the approach of Altug and Hair may some times overestimated \bar{X} in comparison to TMS method.

In the Kobatake's and Nagasawa's method of charge density evaluation the derivations are based on the thermodynamics of irreversible process which has its own limitations. They have claimed that their data of membrane potential on an oxidized collodion membrane, as well as those of previous workers, are fitted quite accurately by the equation derived by them. They have also stated that no such agreement with experiment was obtained in terms of the earlier theory of TMS. These theoretical predictions form the Kobatake and Nagasawa's approaches for charge density evaluation based on thermodynamics of irreversible processes are more accurate as compared to earlier theories of membrane potential.

The Aizawa et al. method is an extended form of Nagasawa et al. approaches for charge density evaluation. The Aizawa et al. access is also based on thermodynamics of irreversible processes. This is also a good method for the evaluation of thermodynamically effective fixed charge density.

In this way the effective fixed charge density and others parameters of the membranes, not only confirms the existence of theories but also best characterized the membranes for their applications.

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Chapter - VI

Studies of Membrane Selectivity for Metal Ions

Introduction

The total electric potential difference observed under zero current flow between two aqueous solutions separated by a membrane has been one of the most widely characterized electrochemical and bio-electric phenomena¹⁻⁸. The fixed charge concept of Teorell⁹, Meyer and Sievers¹⁰ for the charged membranes is a pertinent starting point for the investigation of actual mechanism of ionic or molecular processes which occur in the membrane phase. For biological membranes the electrical potential difference is usually described in terms of Goldman - Hodgkin - Katz^{11,12} equation whereas for certain ion exchange membranes permeable solely to species of one sign, it is described by a generalized Nernst equation. Both Goldman-Hodgkin-Katz and Nernst equation contain ionic permeability ratio terms. Depending on the transport mechanism or the assumption made in the derivation, the permeability ratio has been given various physical meanings as : mobility ratio¹³, ion exchange equilibrium constant¹⁴, the product of the mobility ratio and the Donnan ratio^{9,10}, the product of the mobility ratio and the distribution coefficient ratio¹², the product of the mobility ratio and ion exchange equilibrium constant^{15,16} or the product of the equivalent conductance ratio and the ratio of partition coefficients¹⁷. Sandblom and Eisenman^{1,17,18} have discussed the significance and implication of the observed permeability ratio. Recently a number of reviews have also been appeared dealing with the ion selectivity of membranes¹⁹⁻³⁶.

In this chapter effective fixed charge density of the parchment supported lead tungstate membrane and hen egg (*Gallus saneratii*) shell biological

membrane has been used individually to calculate theoretical bi-ionic potentials (BIP) and compared with experimental determined values. The observed bi-ionic potential values across the lead tungstate and hen egg shell membranes are used for the evaluation of membrane selectivity for metal ions. Membrane conductance values in contact with various 1:1 electrolytes have also been experimentally determined to substantiate our findings. The bi-ionic potential is of great interest in biology and acquires increasing interest in industrial practice.

The theory of absolute reaction rates has also been utilized for the evaluation of Arrhenices activation energy E_a , and the change of enthalpy ($\Delta H^\#$), entropy ($\Delta S^\#$) and free energy ($\Delta F^\#$) of activation by making use of conductance data observed for membrane in contact with various monovalent electrolytes. On the basis of the magnitude of these thermodynamic activation parameters, the selective membrane behaviour has also discussed in the light of an advanced theory of membrane selectivity³⁷.

Experimental

The parchment supported lead tungstate membrane was prepared by the method of the interaction as described earlier in chapter V and hen egg shell membrane was isolated from the freshly laid hen egg (*Gallus saneratii*). The bi-ionic potentials across these membranes were determined by constructing an electrochemical cell of the following type :



The reference electrodes used were reversible saturated calomel electrode ($\text{Hg}/\text{Hg}_2\text{Cl}_2$) connected to the solution via KCl -Agar bridges. A digital multimeter (Rish Multi[®] 4 $\frac{3}{4}$ Digits 18 S) was used to measure values of bi-ionic potential. The bi-ionic potential measurements were carried out either by keeping the concentration of both the electrolytes same on the two sides of the membrane, or by maintaining the concentration of one of the electrolytes constant changing that of the other. Aqueous solution of sodium, potassium and lithium chlorides (BDH, AR grade) were taken in the investigations. The solution on both sides of the membrane were vigorously stirred with a pair of electrically operated magnetic stirrers to remove completely or at least to minimize the effect of film-control diffusion³⁸.

For the measurement of electrical conductivity, membrane was first dipped and equilibrated in an appropriate electrolyte solution. It was then clamped between two half cells and measurements were made according to Fig.(6.1) using a conductivity bridge (Cambridge Instrument Company Ltd., England). All measurements were carried out at $25 \pm 0.1^\circ\text{C}$. The error in measurement of bi-ionic potential was within 1.0% whereas the electrical conductance could be measured to better than 99.5% accuracy.

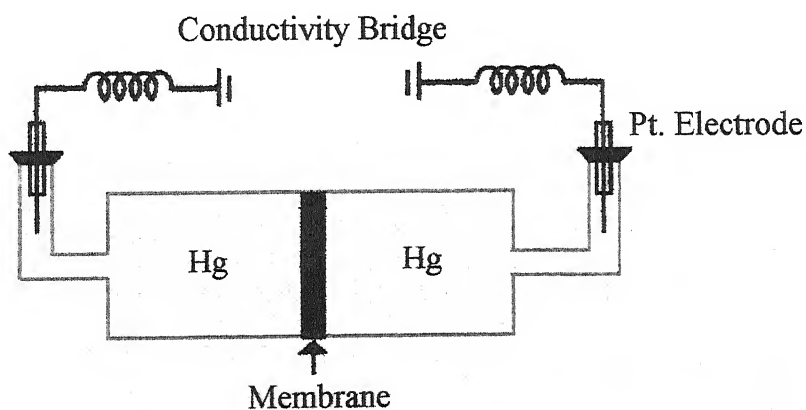


Fig. 6.1

Cell for measuring the electrical conductance of the membrane.

Results and Discussion

When an ion exchange membrane of different concentrations is interposed between two solutions of an electrolyte the mobile species penetrate the membrane and various transport phenomena are introduced into the system³⁹. An electrical potential called a concentration or membrane potential is generated across the membrane. The sign and magnitude of this emf directs the selectivity of the membrane towards the ions of the electrolyte. The value of membrane potential observed experimentally across both the inorganic precipitate parchment supported lead tungstate and hen egg shell biological membranes by taking dilute side positive are given in Table 5.1 and 5.2 respectively in Chapter V. The variation of membrane potential with the change of electrolyte concentrations for various 1:1 electrolytes are also shown in Figs. (5.1 - 5.2) in Chapter V. In both the figures it has been found that membrane potential values decrease with increase in electrolyte concentration and thus on the basis of these potential values membranes follow the sequence of the selectivity of metal ion:



The selectivity sequence of a lead tungstate and hen egg shell membranes, for metal ions of the same sign, can be confirmed by various experimental methods some of the most widely used methods are :

Bi-ionic Method :

If the membrane is used to separate the solution of the AX and BX (or AX and AY) type electrolytes, the steady potential developed is called bi-ionic potential⁴⁰ which is a measure of the selectivity of the membrane for ions of the same sign. This method involves measurement of electrical potentials generated by keeping the same concentration of the ionic species on the two sides of the membrane. For examining the concentration dependence in a bi-ionic experiment, the concentration on the two sides have to change in equal amounts. Bi-ionic potential (E_{BIP}) has been considered by Helfferich¹⁵, according to the concepts of

the TMS theory,^{9,10} as being the algebraic sum of two interfacial potentials and an internal diffusion potential. The mechanisms of bi-ionic potential was considered in detail by Sollner^{41, 42}. He found that not only the relative mobility of the counter ions was important but also the selectivity of the membrane material equally played significant role. According to his views, when the membrane is fixed in a bi-ionic cell, one ion is preferred to the same extent as the membrane is equilibrated with mixed solution containing both counter ions. A complete mathematical discussion under conditions of (a) membrane diffusion control, (b) film diffusion control, and (c) coupled membrane film diffusion control, has been presented. For a general case that involves complete membrane diffusion control the total bi-ionic potential E_{BP} for counterions of equal valance is given by

$$E_{BP} = \frac{RT}{F} \ln \frac{\bar{D}_i a'_i \bar{\tau}_j}{\bar{D}_j a''_j \bar{\tau}_i} \quad (6.1)$$

where a'_i / a''_j , \bar{D}_i / \bar{D}_j , $\bar{\tau}_i / \bar{\tau}_j$ are the activity ratios of the solutions, diffusion coefficient of ions in the membrane phase, and the ratio of the activity coefficients of ions. The symbols R,T,Z and F have their usual meanings. Equation (6.1) reduces in the form of eqn. (6.2) given by Wyllie and Kanaan^{43, 44} :

$$E_{BP} = \frac{RT}{F} \ln \frac{a_i \bar{U}_i}{a_j \bar{U}_j} \quad (6.2)$$

provided $\bar{\tau}_i = \bar{\tau}_j$ and the diffusion coefficients are replaced by mobilities⁴⁴.

Wyllie⁴³ expressed the intramembrane mobility ratio as

$$\frac{\bar{U}_i}{\bar{U}_j} = \frac{\bar{t}_i}{\bar{t}_j} = \frac{\bar{m}_i \bar{\lambda}_i}{\bar{m}_j \bar{\lambda}_j} \quad (6.3)$$

where \bar{t}_i / \bar{t}_j is the intramembrane transference ratio and \bar{m}_i and \bar{m}_j are the steady-state equilibrium concentration of i and j in the respective junction zone ; $\bar{\lambda}_i$ is the conductivity of the membrane when it is wholly in i form and $\bar{\lambda}_j$ is the conductivity of the membrane when it is wholly in j form. Furthermore, it was

shown that $\bar{m}_i / \bar{m}_j \approx K_{ji}$, the selectivity. This, on substitution into eq. (6.3), gives

$$\frac{\bar{U}_i}{\bar{U}_j} = K_{ji} \left(\frac{\lambda_i}{\lambda_j} \right) \quad (6.4)$$

thus the ratio of mobilities were related to the chemical and electrical properties of the membrane.

Bi-ionic potential measurements were also carried out by interposing the membrane between two different electrolyte solutions at the same concentration. The BIP values were low when the membrane was used to separate concentrated electrolyte solutions where as it increased with decreasing salt concentrations. The values of bi-ionic potential across parchment supported lead tungstate membrane and hen egg shell biological membrane with various 1:1 electrolyte combinations at different concentration are given in Tables 6.1-6.2 and plotted in Figs. (6.2 - 6.3). Equation (6.2) was used to calculated the intramembrane mobility ratio \bar{U}_i / \bar{U}_j . The values of \bar{U}_i / \bar{U}_j thus calculated are given in Tables 6.3 - 6.4.

Table 6.1

Experimentally observed values of bi-ionic potential E_{BIP} (mV) across parchment supported lead tungstate membrane at $25 \pm 0.1^\circ\text{C}$

Concentration (Mol / l)	Electrolyte pair		
	KCl-NaCl	KCl-LiCl	NaCl-LiCl
0.1/0.1	6.4	1.2	6.9
0.05/0.05	7.1	1.6	7.4
0.02/0.02	8.5	2.9	9.0
0.01/0.01	10.3	5.5	12.1
0.005/0.005	11.6	7.3	17.8
0.002/0.002	12.1	7.6	19.0
0.001/0.001	12.3	8.1	18.9

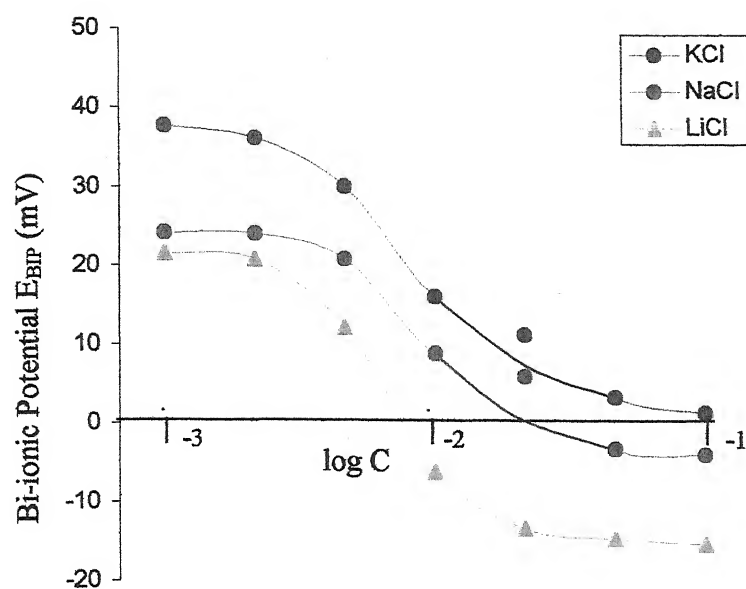


Fig. 6.2

Plots of bi-ionic potential E_{BIP} (mV) against $\log C$ for lead tungstate membrane using 1:1 electrolyte pairs.

Table 6.2

Experimentally observed values of bi-ionic potential E_{BIP} (mV) across hen egg shell membrane at $25 \pm 0.1^\circ\text{C}$

Concentration (Mol / l)	Electrolyte pair		
	KCl-NaCl	KCl-LiCl	NaCl-LiCl
0.1/0.1	1.3	-5.0	-4.0
0.05/0.05	1.9	-2.5	-1.5
0.02/0.02	2.7	-0.6	0.6
0.01/0.01	3.9	2.8	1.1
0.005/0.005	5.10	6.2	1.8
0.002/0.002	8.9	9.7	2.4
0.001/0.001	10.3	12.2	4.5

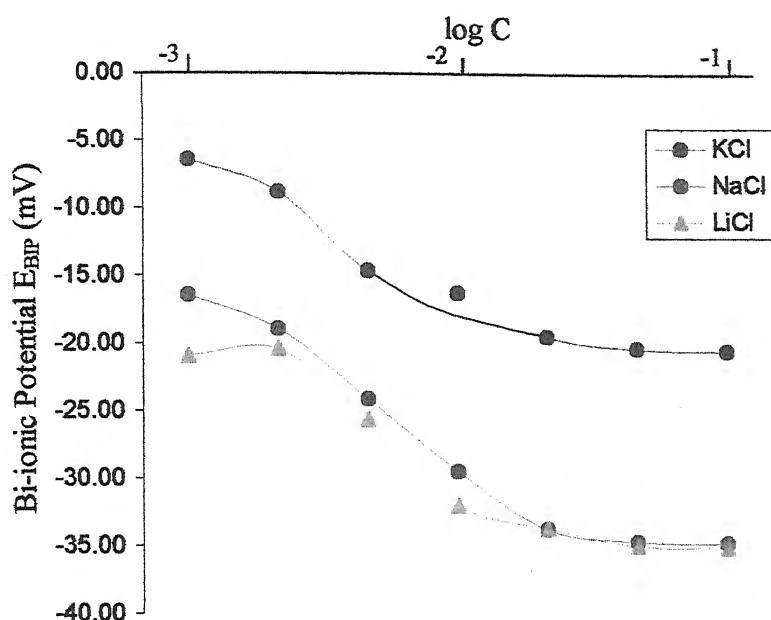


Fig. 6.3

Plots of bi-ionic potential E_{BIP} (mV) against $\log C$ for hen egg shell membrane using 1:1 electrolyte pairs.

An interesting point with regard to the value of \bar{U}_i/\bar{U}_j is that the mobility ratio undergoes considerable change with the concentration of the external solutions and this behavior was seen with each electrolyte pair.

To gain knowledge of selectivity K_{ij} from the predetermined values of \bar{U}_i/\bar{U}_j , the ratio of electrical conductivities $\bar{\lambda}_i/\bar{\lambda}_j$, demanded by eqn. (6.4), must be known. Membrane conductance measurements were carried out when it was wholly in form i or form j. The values of membrane conductance at various electrolyte concentrations are given in Tables (6.5 - 6.6). These values are relatively more dependent on the concentration of the electrolytes within the membrane as shown in Figs. (6.4-6.5).

Table 6.3

Values of the intermembrane mobility ratio of various 1:1 electrolyte ion pairs across parchment supported lead lungstate membrane.

Concentration (Mol / l)	Electrolyte ion pair		
	$\bar{U}_{K^+} / \bar{U}_{Na^+}$	$\bar{U}_{K^+} / \bar{U}_{Li^+}$	$\bar{U}_{Na^+} / \bar{U}_{Li^+}$
0.1/0.1	1.01	1.33	1.18
0.05/0.05	1.03	1.34	1.23
0.02/0.02	1.10	1.52	1.42
0.01/0.01	1.22	1.75	1.76
0.005/0.005	1.28	1.98	1.84
0.002/0.002	1.37	2.21	1.94
0.001/0.001	1.53	2.38	1.98

Table 6.4

Values of the intermembrane mobility ratio of various 1:1 electrolyte ion pairs across hen egg shell membrane.

Concentration (Mol / l)	Electrolyte pair		
	$\bar{U}_{K^+} / \bar{U}_{Na^+}$	$\bar{U}_{K^+} / \bar{U}_{Li^+}$	$\bar{U}_{Na^+} / \bar{U}_{Li^+}$
0.1/0.1	0.93	1.12	1.11
0.05/0.05	1.05	1.13	1.12
0.02/0.02	1.16	1.31	1.26
0.01/0.01	1.34	1.59	1.43
0.005/0.005	1.43	1.65	1.50
0.002/0.002	1.53	1.86	1.64
0.001/0.001	1.60	2.02	1.83

Table 6.5

Experimentally observed values of membrane electrical conductance (mhos) across parchment supported lead tungstate membrane for monovalent electrolytes at $25 \pm 0.1^\circ\text{C}$

Concentration (Mol / l)	Electrolyte		
	KCl	NaCl	LiCl
0.1/0.1	8.6×10^{-2}	7.1×10^{-2}	6.3×10^{-2}
0.05/0.05	5.2×10^{-2}	4.5×10^{-2}	3.74×10^{-2}
0.02/0.02	3.2×10^{-2}	2.7×10^{-2}	2.1×10^{-2}
0.01/0.01	2.41×10^{-2}	1.7×10^{-2}	1.2×10^{-2}
0.005/0.005	1.91×10^{-2}	1.2×10^{-2}	0.7×10^{-2}
0.002/0.002	1.39×10^{-2}	0.81×10^{-2}	0.4×10^{-2}
0.001/0.001	0.93×10^{-2}	0.51×10^{-2}	0.20×10^{-2}

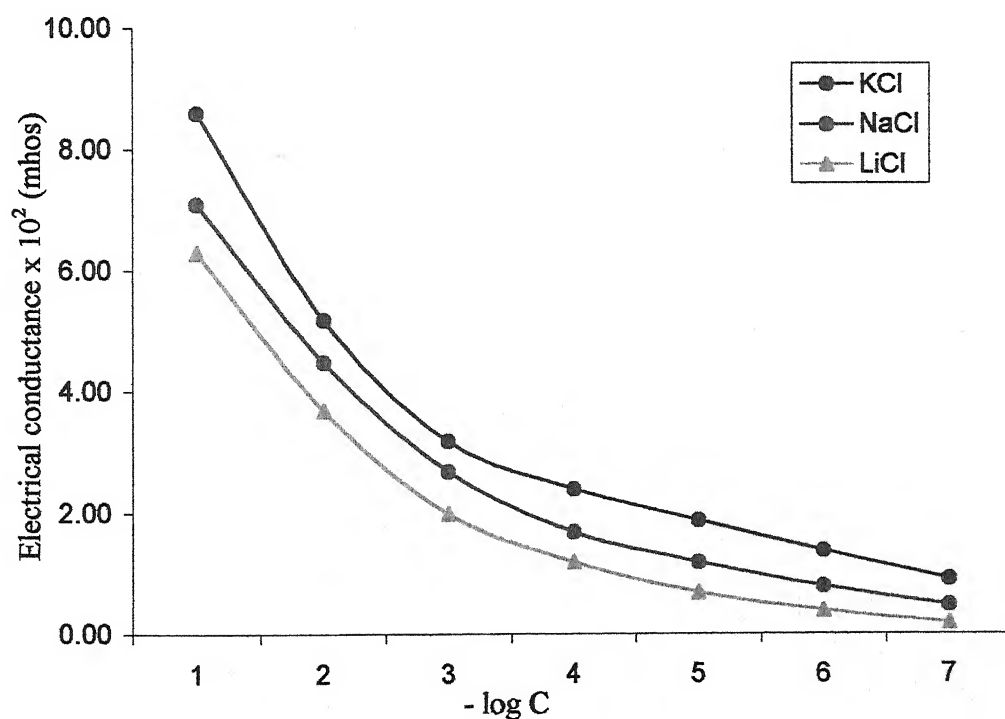


Fig. 6.4

Plots of conductance $\times 10^2$ (mhos) Vs. $-\log C$ for lead tungstate membrane with 1:1 electrolytes.

Table 6.6

Experimentally observed values of membrane electrical conductance (mhos) across hen egg shell membrane for monovalent electrolytes at $25 \pm 0.1^\circ\text{C}$

Concentration (Mol / l)	Electrolyte		
	KCl	NaCl	LiCl
0.1/0.1	5.3×10^{-2}	4.8×10^{-2}	4.3×10^{-2}
0.05/0.05	4.6×10^{-2}	4.0×10^{-2}	3.5×10^{-2}
0.02/0.02	3.1×10^{-2}	2.7×10^{-2}	2.3×10^{-2}
0.01/0.01	2.3×10^{-1}	2.0×10^{-2}	1.8×10^{-2}
0.005/0.005	1.80×10^{-2}	1.51×10^{-2}	1.38×10^{-2}
0.002/0.002	0.5×10^{-2}	0.3×10^{-2}	0.13×10^{-2}
0.001/0.001	0.3×10^{-2}	0.2×10^{-2}	0.11×10^{-2}

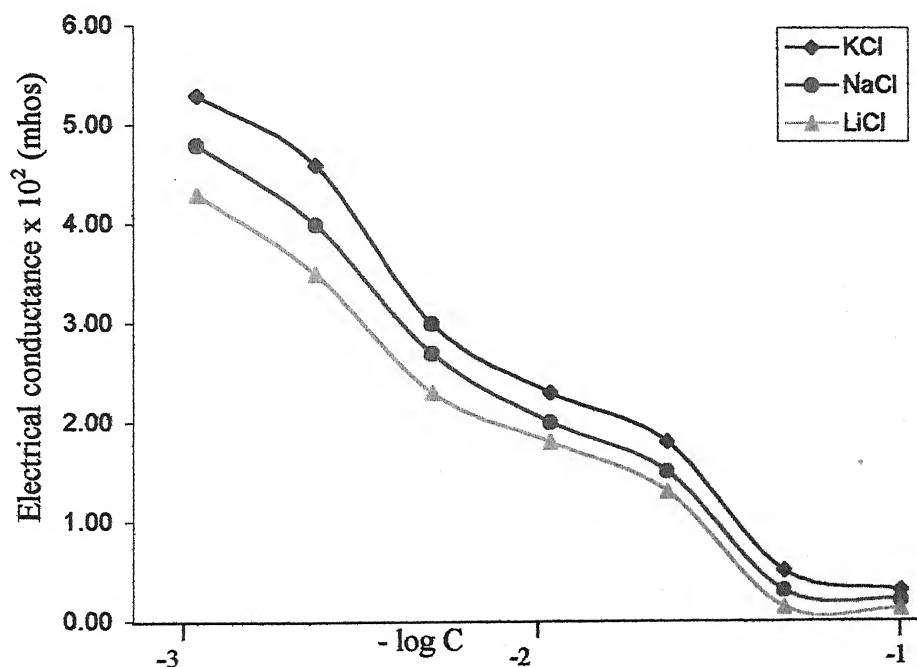


Fig. 6.5

Plots of conductance $\times 10^2$ (mhos) Vs. $-\log C$ for hen egg shell membrane with 1:1 electrolytes.

This implies that the membranes have a relatively high Donnan uptake of anion and a low selectivity constant value. The values of selectivity K_{ij} evaluated from the mobilities ratio and the ratio of electrical conductivities using the data from Tables (6.3-6.4) and (6.5-6.6) are given in Tables (6.7-6.8). The intramembrane mobility ratio values also refer to the selectivity sequence of the membrane for the cations : $K^+ > Na^+ > Li^+$

Table 6.7

Values of selectivity $K_{ji} \simeq (1 / S_{ij})$ evaluated from intramembrane mobility ratio and the ratio of electrical conductivities at various electrolyte concentrations for parchment supported lead tungstate membrane.

Concentration (Mol / l)	Selectivity		
	K_{NaK}	K_{LiK}	K_{LiNa}
0.1/0.1	0.82	1.01	1.08
0.05/0.05	0.88	1.06	1.10
0.02/0.02	0.97	1.31	1.31
0.01/0.01	1.10	1.57	1.40
0.005/0.005	0.91	1.26	1.62
0.002/0.002	1.26	1.92	1.81
0.001/0.001	1.39	1.66	1.48

Table 6.8

Values of selectivity $K_{ji} \simeq (1 / S_{ij})$ evaluated from intramembrane mobility ratio and the ratio of electrical conductivities at various electrolyte concentrations for hen egg shell membrane.

Concentration (Mol / l)	Selectivity		
	K_{NaK}	K_{LiK}	K_{LiNa}
0.1/0.1	1.05	0.56	0.59
0.05/0.05	1.08	0.58	0.63
0.02/0.02	1.23	0.68	0.70
0.01/0.01	1.24	0.72	0.68
0.005/0.005	1.56	0.75	0.73
0.002/0.002	2.06	1.12	0.98
0.001 / 0.001	2.08	1.22	1.04

This order of selectivity on the basis of the Eisenman-Sherry model of membrane selectivity^{45,46} points towards the weak field strength of the charge groups attached to the membrane matrix. This is in accordance with an earlier finding of charge density determinations of lead tungstate and hen egg shell membranes, which have already been reported in previous chapter-V of this thesis.

In a number of theoretical papers^{1,17,18,23,39,45,47} different aspects of ion permeation in various membrane systems have been published. From thermodynamic treatment Sandblom and Eisenman¹⁸ derived the eqn. (6.5)

$$\frac{P_i}{P_j} = K_{ji} \frac{\bar{U}_i}{\bar{U}_j} \quad (6.5)$$

for fixed site membranes which implies that the permeability ratio is quite generally related to the ion exchange equilibrium constant K_{ij} and the ratio of mobilities of the critical ions, where K_{ij} is the ion exchange equilibrium constant defined by $K_{ji} = 1/K_{ij} = a_j c_i / a_i c_j$.

Equation (6.5) suggests that the permeability ratio P_i/P_j can be calculated, provided that the mobility ratio \bar{U}_i/\bar{U}_j and the ion exchange constant K_{ij} of a membrane for the ions are known the values of permeability ratio derived in this way form the predetermined values of \bar{U}_i/\bar{U}_j and K_{ij} for lead tungstate membrane are given in Tables (6.9-6.10). The data in Tables (6.9-6.10) show that the membranes are weakly selective and that the selectivity increases with a decrease in the concentration of the bathing solutions. This is in full agreement with our earlier findings of membrane potential measurements with inorganic precipitate membranes^{19, 23}.

Table 6.9

Values of permeability ratio (P_i / P_j) across parchment supported lead tungstate membrane for monovalent electrolytes at various concentrations.

Concentration (Mol/l)	Permeability ratio		
	P_{K^+} / P_{Na^+}	P_{K^+} / P_{Li^+}	P_{Na^+} / P_{Li^+}
0.1/0.1	0.82	1.28	1.33
0.05/0.05	0.93	1.35	1.41
0.02/0.02	1.08	1.84	1.98
0.01/0.01	1.34	2.46	2.75
0.005/0.005	1.47	2.93	2.50
0.002/0.002	1.58	3.49	3.21
0.001 / 0.001	1.91	3.78	3.94

Table 6.10

Values of permeability ratio (P_i / P_j) across hen egg shell membrane for monovalent electrolytes at various concentrations

Concentration (Mol/l)	Permeability ratio		
	P_{K^+} / P_{Na^+}	P_{K^+} / P_{Li^+}	P_{Na^+} / P_{Li^+}
0.1/0.1	1.0	0.8	0.8
0.05/0.05	1.1	0.9	0.9
0.02/0.02	1.2	0.96	1.0
0.01/0.01	1.3	1.0	1.10
0.005/0.005	1.6	1.2	1.2
0.002/0.002	2.1	1.6	1.3
0.001 / 0.001	2.2	1.9	1.4

One Sided Addition Method :

In this method measurement of bi-ionic potentials are carried out by keeping the concentration of one of the electrolyte (AX) constant and varying the concentration of other electrolyte (BX), and then by keeping the concentration of electrolyte BX constant and varying that of AX.

Bi-ionic potential^{40,48} is also defined again as the membrane potential across a membrane which separates two electrolyte solutions with different concentrations, i.e. different mobile ions carrying the charge opposite to the fixed charge on the membrane. The emf (bi-ionic potential) of the membrane has been related to the fixed charge concentration (ϕX) by the equation :

$$E_{BIP} = \frac{RT}{F} \ln \frac{\sqrt{1 + (\phi_X M_A / 2a)^2} - (\phi_X M_A / 2a)}{\sqrt{1 + (\phi_X M_B / 2a)^2} - (\phi_X M_B / 2a)} \quad (6.6)$$

where $\phi_X M_A$ and $\phi_X M_B$ are the concentrations of the fixed ions on the membrane phase. Equation (6.6) can be used to calculate bi-ionic potential across a membrane provided effective fixed charge density of the membrane and the concentration of external electrolyte solutions are known. The values of bi-ionic potential thus derived using predetermined values of effective fixed charge density of the membranes are given in Tables (6.11 - 6.12). For comparison the observed values are also given in the same tables. These values are closer to each other.

Table 6.11

Theoretical and experimentally observed values of bi-ionic potential E_{BIP} (mV) across parchment supported lead tungstate membrane.

Electrolyte Pair	Experimental			Theoretical		
	KCl-NaCl	KCl-LiCl	NaCl-LiCl	KCl-NaCl	KCl-LiCl	NaCl-LiCl
concentration (Mol / l)						
0.1/0.1	6.4	1.2	6.9	6.0	1.1	6.2
0.05/0.05	7.1	1.6	7.4	6.7	2.1	7.6
0.02/0.02	8.5	2.9	9.0	9.1	3.2	11.2
0.01/0.01	10.3	5.5	12.1	11.1	5.9	12.8
0.005/0.005	11.6	7.3	17.8	12.2	7.9	18.3
0.002/0.002	12.1	7.6	19.0	12.8	8.14	19.1
0.001/0.001	12.3	8.1	18.9	12.9	8.8	19.5

Table 6.12

Theoretical and experimentally observed values of bi-ionic potential E_{BIP} (mV) across hen egg shell membrane.

Electrolyte Pair	Experimental			Theoretical		
	KCl-NaCl	KCl-LiCl	NaCl-LiCl	KCl-NaCl	KCl-LiCl	NaCl-LiCl
concentration (Mol / l)						
0.1/0.1	1.3	-5.0	-4.0	1.6	-4.4	-4.1
0.05/0.05	1.9	-2.5	-1.5	2.0	-2.5	-1.8
0.02/0.02	2.7	-0.6	0.6	2.5	-0.5	-0.5
0.01/0.01	3.9	2.8	1.1	3.7	2.7	1.4
0.005/0.005	5.1	6.2	1.8	5.3	6.0	1.7
0.002/0.002	8.9	9.7	2.4	8.1	9.3	2.3
0.001/0.001	10.3	12.2	4.5	9.8	11.1	3.9

It is well known that bi-ionic potential is a measure of selectivity⁴⁹ of membrane for ions of the same sign. Equation (6.7) has been found to predict similar to eqn. (6.1) the values of bi-ionic potential reasonably well, provided $\bar{\tau}_B / \bar{\tau}_A$ remains constant :

$$E_{BIP} = \frac{RT}{F} \ln \frac{\bar{U}_{Aa'_A} \bar{\tau}_B}{\bar{U}_{Ba''_B} \bar{\tau}_A} \quad (6.7)$$

This equation can be written as

$$E_{BIP} = \frac{RT}{F} \ln \frac{\bar{U}_{Aa'_A}}{\bar{U}_{Ba''_B}} \text{ (if } \bar{\tau}_A = \bar{\tau}_B \text{)} \quad (6.8)$$

and

$$E_{BIP} = \frac{RT}{F} \ln \frac{\bar{\tau}_A}{\bar{\tau}_B} \quad (6.9)$$

Where

$$\frac{\bar{t}_A}{\bar{t}_B} = \frac{\bar{U}_{Aa'_A} \bar{\tau}_B}{\bar{U}_{Ba''_B} \bar{\tau}_A}$$

provided that the Donnan ratio $\bar{a}_A / \bar{a}_B = \bar{a}_{A'} / \bar{a}_{B'}$ is established.

The bi-ionic potential generated across lead tungstate and hen egg shell membranes were measured keeping the concentration of AX constant and by varying concentration of BX, and again by keeping BX constant and varying AX. These measurements were extended to three solution pairs, i.e. KCl-NaCl, KCl-LiCl and NaCl-LiCl. The bi-ionic potentials thus measured are given in Tables (6.13-6.14). These values are also shown in Figs. (6.6-6.7) as a function of $\log a_{AX}/a_{BX}$. Good straight lines as demanded by eqn. (6.8) are obtained. The potential of intersection of the two straight lines at the same activity, i.e. $a_{AX}/a_{BX}=1$, given the value of transport ratio using eqn. (6.9). The transport ratio thus obtained for different 1:1 electrolyte pairs for lead tungstate and hen egg shell membranes are given in Table 6.15.

Table 6.13

Experimental values of bi-ionic potential across parchment supported lead tungstate membrane keeping the concentration of one electrolyte constant and varying the concentration of other electrolyte and vice- versa

Concentration (Mol/l)	Electrolyte Pair					
	KCl-NaCl	NaCl-KCl	NaCl-LiCl	LiCl-NaCl	KCl-LiCl	LiCl- KCl
0.1/0.5	15.6	1.6	10.4	-4.8	9.8	-4.3
0.1/0.01	19.3	-10.2	21.3	-20.2	18.3	-16.2
0.1/0.005	25.10	-18.9	31.5	-31.5	26.9	-24.4
0.1/0.001	30.3	-20.5	40.1	-42.6	35.8	-33.3

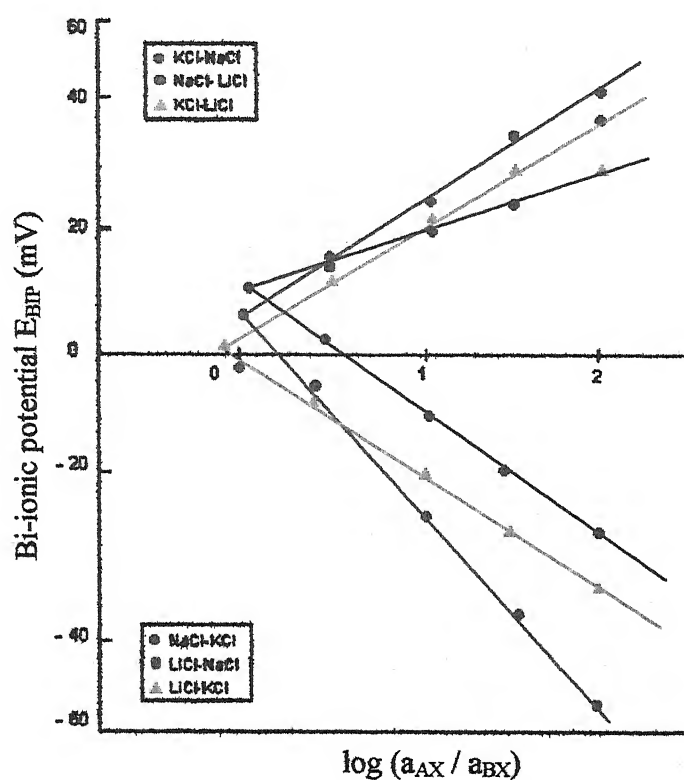


Fig. 6.6

Plots of bi-ionic potential E_{BIP} (mV) against $\log (a_{AX} / a_{BX})$ for lead tungstate membrane.

Table 6.14

Experimental values of bi-ionic potential across hen egg shell membrane keeping the concentration of one electrolyte constant and varying the concentration of other electrolyte and vice-versa

Concentration (Mol/l)	Electrolyte Pair					
	KCl-NaCl	NaCl-KCl	NaCl-LiCl	LiCl-NaCl	KCl-LiCl	LiCl-KCl
0.1/0.5	4.2	-11.9	10.2	-13.8	7.2	-15.3
0.1/0.01	23.6	-24.8	28.8	-32.6	17.3	-27.9
0.1/0.005	36.10	-33.3	45.3	-45.4	28.4	-40.2
0.1/0.001	50.0	-45.2	60.1	-56.9	35.4	-50.4

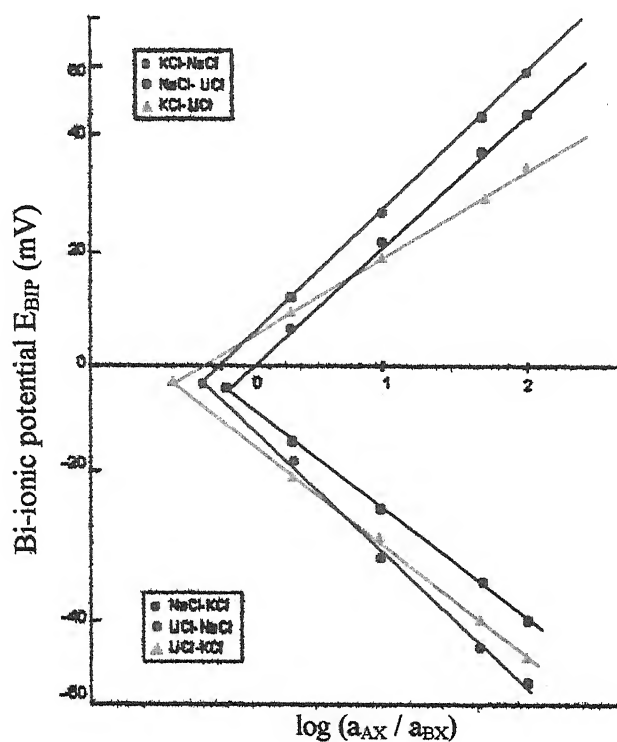


Fig. 6.7

Plots of bi-ionic potential E_{BIP} (mV) against $\log (a_{AX} / a_{BX})$
for hen egg shell membrane

Table 6.15

Values of transport ratio obtained for different 1:1 electrolyte pairs across the parchment supported lead tungstate and hen egg shell membranes

Membranes	Transport ratio		
	t_{K^+} / t_{Na^+}	t_{K^+} / t_{Li^+}	t_{Na^+} / t_{Li^+}
Lead Tungstate	1.13	1.09	1.08
Hen egg shell	1.5	1.2	1.10

These results also point towards the order of selectivity of cations transporting through the membranes is as follows.

$$K^+ > Na^+ > Li^+$$

Absolute Reaction Rates Methods :

In this method the theory of reaction rates was applied to the diffusion of ions through both the membranes and its application to the membrane conductance data for investigate the mechanism of ion transport and for the calculation of various thermodynamic parameters. viz. E_a , ΔF^\ddagger , ΔH^\ddagger and ΔS^\ddagger . In order to substantiate our findings and further to understand the selectivity of membranes in energetic terms the values of various activation parameters have been evaluated on the basis of rate theory. The need for the use of rate theory has been felt because, electrical measurements carried out for assessing selectivity involve kinetic contributions to the permeation process and their explanation can not be expected to be given rigorously in terms of equilibrium energetic concepts. The rate theory describes any process from diffusion to chemical reaction in terms of elementary jumps over energy barriers, and can be used to represent the processes of permeation in as much detail than or with as much accuracy as desired. The permeate encounters energy maxima

(barriers) and minima (wells) in its journey form one side of the membrane to the other. The energy maxima represent the energies of the represented by single jumps over the corresponding barrier. The progress over each barrier is proportional to the number of ions attaining the energy needed to cross barrier. The rate constant K_j for crossing over a barrier is related to standard Gibb's Free energy of activation ΔF^\ddagger , by;

$$k_i = A_i \cdot e^{(-\Delta F^\ddagger / RT)} \quad (6.10)$$

where A_i is the frequency of attempted hops. The ΔF^\ddagger is related to enthalpy (ΔH^\ddagger) and entropy (ΔS^\ddagger) of activations by the Gibbs-Helm Holtz equation.

$$\Delta F^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (6.11)$$

ΔH^\ddagger and ΔS^\ddagger can be evaluated with the help of specific conductance, π , by making the use of the work of Eyring^{50, 51}

$$\pi = RT / nh - e^{-\Delta H^\ddagger / RT} e^{\Delta S^\ddagger / R} \quad (6.12)$$

ΔH^\ddagger is related to the Arrhenius energy of activation E_a by

$$E_a = \Delta H^\ddagger + RT \quad (6.13)$$

To use eqn. (6.12) $\log \pi nh / RT$ has been plotted against $1/T$ as shown in Figs. (6.8 - 6.9). The straight line plots confirm the applicability of this equation to our model system and allow the calculation of ΔH^\ddagger and ΔS^\ddagger from the slopes and intercepts of the linear plots. The parameters so evaluated have been used to calculate the magnitude of ΔF^\ddagger and E_a with the help of eqns. (6.1) and (6.13), respectively. The results of these calculations are summarized in Tables (6.16 - 3.17)

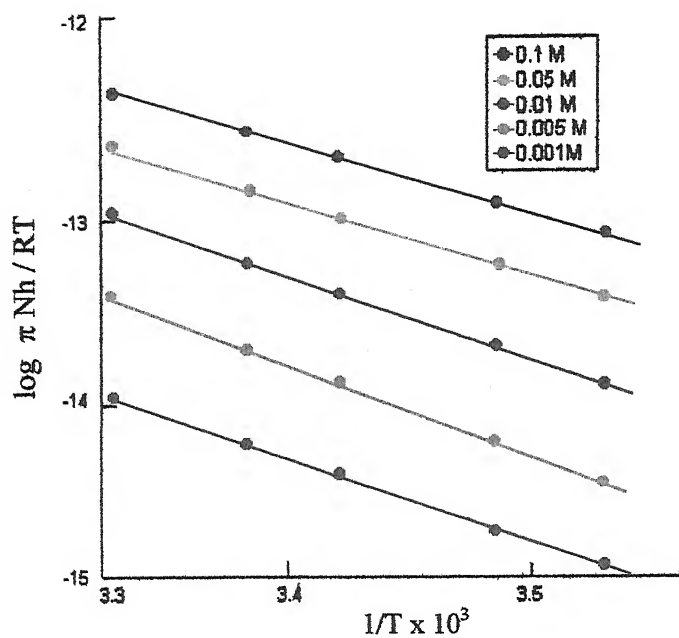


Fig. 6.8

Plots of $\log \pi N_h / RT$ Vs $1/T$ for lead tungstate membrane

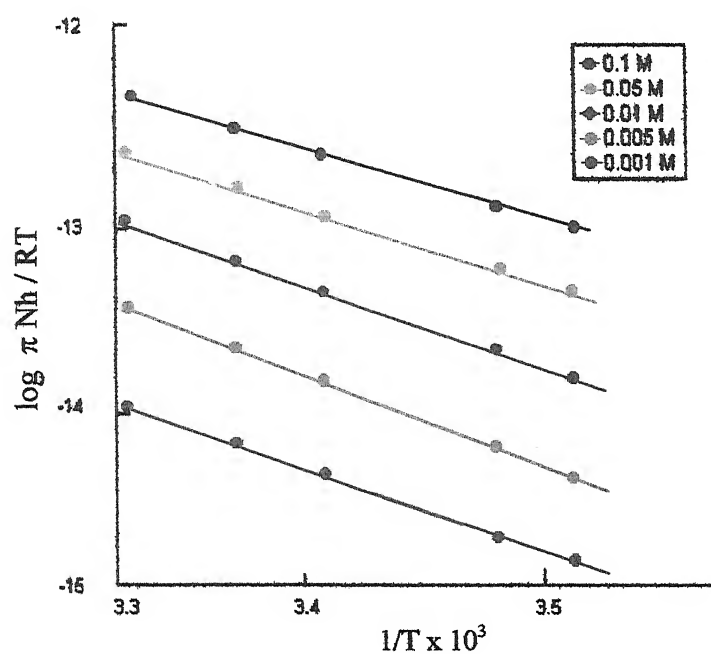


Fig. 6.9

Plots of $\log \pi N_h / RT$ Vs $1/T$ for hen egg shell membrane

Table 6.16

The calculated values of thermodynamic activation parameters for parchment supported lead tungstate membrane evaluated on the basis of absolute reaction rates theory.

Electrolyte Concentration (Mol / l)	Parameters (KCal/Mol)			
	E_a	ΔF^\ddagger	ΔH^\ddagger	$-\Delta S^\ddagger$
KCl				
0.1	1.31	10.81	1.33	14.31
0.05	2.11	13.66	2.74	15.21
0.01	4.12	15.93	3.91	16.71
0.005	5.66	17.11	5.26	17.50
0.001	7.12	18.76	6.51	20.71
NaCl				
0.1	1.12	11.9	1.12	19.21
0.05	2.94	13.28	2.18	19.83
0.01	4.18	15.23	3.33	20.16
0.005	5.36	17.24	4.98	21.38
0.001	6.95	18.25	6.21	23.12
LiCl				
0.1	1.02	11.61	1.02	20.10
0.05	2.93	11.14	2.74	21.33
0.01	4.12	15.54	3.51	22.76
0.005	5.24	17.15	4.76	23.36
0.001	6.18	17.42	9.98	24.26

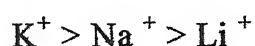
Table 6.17

The calculated values of thermodynamic activation parameters for hen egg shell membrane evaluated on the basis of absolute reaction rates theory .

Electrolyte Concentration (mol/l)	Parameters (KCal / Mol)			
	E_a	ΔF^\ddagger	ΔH^\ddagger	$-\Delta S^\ddagger$
KCl				
0.1	1.51	11.10	1.38	14.10
0.05	2.41	13.73	2.82	15.15
0.01	4.16	15.99	3.97	16.64
0.005	5.72	17.24	5.33	17.09
0.001	7.41	18.83	6.81	20.64
NaCl				
0.1	1.22	11.40	1.17	17.60
0.05	2.99	13.33	2.26	18.23
0.01	4.24	15.42	3.43	19.35
0.005	5.41	17.37	5.14	20.46
0.001	6.71	18.28	6.11	21.38
LiCl				
0.1	1.02	11.81	1.08	20.21
0.05	2.98	11.18	2.85	21.42
0.01	4.28	15.68	3.77	22.88
0.005	5.64	17.29	4.89	23.53
0.001	6.39	18.84	9.97	24.46

The size dependence of the magnitude of E_a , ΔF^* and ΔH^* shows that a larger ion has more difficulty in crossing the membrane than a smaller one. This type of variation can be explained by considering the location of energy peaks and wells and also by comparing the heights of energy barriers (i.e., the difference between outer wells and peaks). It has been found that the larger ion encounters a bigger entrance barrier lying very close to the surface of the membrane. The entrance barrier for the smaller ion is not only to lesser height but also lies farther in³⁷. The location of the outermost well has been assumed to be the same for all the species, while that of the inner well is much farther in for the smaller ion than the larger ones. Keeping in mind these facts, it can be argued that the magnitude of the above mentioned activation parameters should be higher for larger ions than for smaller ones.

The magnitude of ΔS^\ddagger indicates the mechanism of flow and has been interpreted in a number of ways. The negative values of ΔS^\ddagger found for ion permeation through the membranes used in the present investigation are attributable to electrolyte diffusion with partial immobilization in the membrane, the partial immobility increasing with the increase of density of charge on the permeant. This conclusion is in good agreement with the most recent findings of Marcus⁵², who established that the translational immobilization entropy of solvents follows the sequence $\text{Li}^+ > \text{Na}^+ > \text{K}^+$ resulting the selectivity sequence of the membranes for alkali metal ions as :



Conclusion

The parchment supported inorganic precipitate lead tungstate and hen egg shell biological membranes, which are used as the model membranes have been studied thoroughly for their selectivity to the metal ions. On the basis of the result of the experimentally measured values of electrical membranes potential, the selectivity of the metal ions for both the membranes were obtained

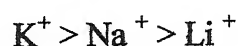
$$K^+ > Na^+ > Li^+$$

Moreover, the selectivity of the membranes was determined by three widely used methods namely : bi-ionic method., one sided method and Absolute reaction rates method. Bi-ionic method involves the measurements of electrical potential by keeping the same concentration on the two sides of the membrane, which were measured across both the membranes using various combination of 1:1 electrolytes at different concentration. The intra membrane mobility and permeability ratios of cations were derived using the plotting method. Conductivity of the membranes in contact with single electrolyte were also determined experimentally in order to evaluate selectivity of the membranes using the predetermined values of intra membrane permeability ratio. The equation of permeability ratio, selectivity constant and the ratio of the individual ionic mobilities derived recently by sandblom and Eisenman from the macroscopic laws of irreversible thermodynamics was used to evaluate various membrane parameters. The selectivity sequence of both the membrane for the cations were of the following order

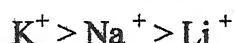
$$K^+ > Na^+ > Li^+$$

In one sided addition method, bi-ionic potential were carried out by keeping the concentration of one of the electrolyte constant and varying the concentration of other electrolyte. Utilizing the best equations of wilson, Wyllie

and Ilani and the data of bi-ionic potential, effective fixed charge density, the evaluated values confirmed the selectivity sequence of membrane alkali metal as :



By using the absolute reaction rates method the selectivity of metal ions of the membranes was also tested in terms of the values of various activation parameters like, : E_a , ΔF^* , ΔH^* and ΔS^* , which were predicted the basis of rate theory. The parameters ΔS^* the entropy of activation represents the mechanism of ion permeation in terms of electrolyte diffusion with partial immobilization in the membrane. The partial immobility causes the selectivity behaviour of membrane for metal ions. In this way the selective membrane behaviour in terms of thermodynamic activation parameters evaluated by utilizing the theory of absolute reaction rate was also found the same :



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Chapter-VII

Membrane Characterisation Using Impedance Measurements

Introduction

Transport phenomena across the membranes both in biological systems and in many industrial processes, are important because of their potential use in various separation processes. Studies on the physicochemical aspects of membranes were started a few decades ago. An excellent monograph by Lakshminarayanaiah covers progress in this field¹

Extensive research work has been started to study the complex behaviour of biological membranes by developing various artificial membranes such as parchment supported inorganic precipitates which may mimic some properties of biological membranes *in vivo*²⁻¹⁰. Among the various theories reviewed by Kedem and Katchalsky¹¹ and classified by Schlögl¹². The concept of the theory of rate processes has been applied by various authors^{2,4,13-15} in the study of diffusion phenomena through different membranes.

S.H. White¹⁶ studied the membrane capacitance under various conditions of surface charge and electrolyte concentration. Kobatake et.al.¹⁷ studied the impedance of surface membrane of protoplasmic drops. Membrane capacitance and resistance was found to be frequency dependent. Takashima et al.¹⁸ has shown that the parallel arrangement of resistance and capacitance may be transformed to a series arrangement. A.E. Hill¹⁹ while studying the ion transport through leaf gland cells of limonium measured the impedance characteristics of the whole leaf disc. The frequency characteristics was examined with a.c. bridge circuit. The a.c. response to a rough electrode surface in contact with an aqueous electrolyte has been discussed by de Levie^{20, 21}.

The technique of capacitance has been applied to many passive and excitable membranes²²⁻²⁵. Early works of Cole and Curtis²⁴ and Cole and Baker²⁶ demonstrate various unique features of nerve membranes. The analysis indicate that the effect of electrolyte concentration and bridge frequency on membrane capacitance is not due to electrode polarization but may be due to some structural changes in the membrane as discussed by Vallejo et al.²⁷. The frequency dependence of the electrical impedance of a tissue is conveniently represented by the impedance locus, a graph of reactive component against resistive component with frequency as implicit parameter. The impedance locus of a cell membrane is frequently a circular arc with its center below the resistance axis.²⁸

A number of theoretical point charge²⁹⁻³⁴ and finite ion size model^{20,21,35} for the solid/electrolyte conductor interface have been used to interpret the impedance characteristics under various conditions of blocked, partially blocked and unblocked electrolyte depending upon the extent of penetration of the electrolyte to the electrode.^{20,21} Armstrong³⁵ has attempted to use some of the theoretical models for aqueous electrolyte systems in order to obtain a simple model for the metal/superior conductor interphase which can explain some of the experimental observations that have been made on these systems³⁵.

In majority of cases, an electrochemical cell is better understood by a complicated network of resistance and capacitance. These show a complex behaviour in the complex impedance plane. If an impedance spectrum is given, one can calculate the components of an equivalent circuit of resistance and capacitance responsible for it. Thus with the measurements on electrochemical cells, It is usual for investigator to measure the impedance of the cell and subsequently to find the probable equivalent circuit and the significance of different components. This is usually carried out by comparing the results with the theoretical model.

Application of a.c impedance methods to study the electrical properties of primarily ion-conducting membranes used in ion selective electrodes resulted in data which could not be fully interpreted on the basis of available theory at that time³⁶. Published data on similar systems were treated by different models.³⁷⁻⁴¹ Since adequate interpretation of these data is essential for an understanding of fixed-site membrane phenomena. Impedance measurements provide a powerful diagnostic tool for the analysis of many electrochemical systems⁴²⁻⁴⁵. In order to understand the behavior of complex living membranes, simple polymeric for some time⁴⁶ liquid bilayer membranes.⁴⁷⁻⁴⁸, parchment and millipore filter paper supported membranes^{47,49-51} and composite membranes⁵²⁻⁵⁴ in recent years have been used as models by a number of investigators.

Buck and Krull³⁶ measured impedances of several glass membrane electrodes from about 0.1 Hz to just under 100 KHz. Complex-plane impedance plots (absolute Z_o vs. Z_R) of their data, as advocated for electrochemical systems by Sluyters et al.⁵⁵, showed for each glass what appeared to be a skewed semicircle at high frequencies with the beginning of another arc at lower frequencies. Bluck⁵⁶ interpreted the high frequency data in terms of bulk properties and geometric capacitance of the glasses while the low frequency data were thought to depend upon an interfacial phase such as a hydrated film at the surfaces.

Buck⁵⁶ proposed the two section equivalent circuit shown in Fig. (7.1) in which R_∞ was the high frequency bulk resistance of the glass, C was the double layer geometric capacitance and Z_1 was an infinite transmission line or Warburg⁵⁷ diffusion impedance. This left portion of the circuit was thought to correspond to the bulk high frequency properties of the glass while Z_2 was a finite transmission line, representing mobile cation and anion transport through an interfacial phase such as a hydrated film.

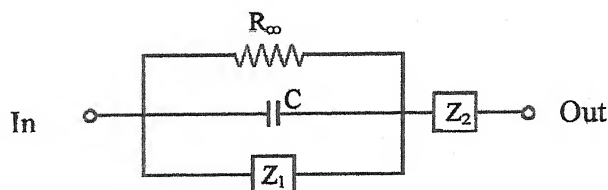


Fig. 7.1

Two section equivalent circuit

Buck⁵⁶ summarized the abundant chemical evidence for the existence of such films. The low frequency response was assumed to be determined by Z_2 which was modeled on the diffusion impedances of galvanic cell having closely spaced electrodes. The form of Z_2 had been previously derived by a number of workers,^{55,56,58-60} and verified experimentally by Sluyters^{55,60} for the case of diffusion-limited current in the presence of inert electrolyte.

Brand and Rechnitz^{61, 62} concluded from their measurements of the impedances of glass electrodes that the low frequency data, again assumed to correspond to a surface film was more accurately described as an infinite transmission line shunted by a resistor. The required value of the shunting resistor was between five and six times the value of the bulk resistance, which implied that the surface film was more resistive than the glass itself. Their low frequency data obtained with 1 volt excitation show considerable scatter, probably from $1/f$ noise^{63,64} and a precise determination of the shunting resistance value was not possible. However Bates⁶⁵ has cited evidence that the resistance of the surface film should be much smaller than the bulk value. Further more, Wikby and Johansson⁶⁶ present even more convincing experimental evidence that the surface film has a resistivity comparable with a solution phase.

Warburg⁵⁷ developed the theory of diffusional impedances and derived the expression for it. The work of Mac Donald⁶⁷ provides a systematic treatment of small signal a.c response of conducting cell and membranes. Armstrong and

Archur⁶⁸ interpreted the complex impedance spectra for solid/electrolyte interfaces.

In this chapter the electrical resistance and capacitance of parchment supported lead tungstate model membrane and hen egg (*Gallus saneratii*) shell biological membrane in contact with aqueous sodium chloride solutions measured at different concentrations and various frequencies have been described. The impedance characteristics, which is an important electrical property governing the membrane phenomena, have been computed. These parameters have been determined in order to substantiate our findings regarding the mechanism of transport through the membranes under investigation with particular reference to its function in different environment.

Experimental

The parchment supported lead tungstate model membrane and hen egg (*Gallus saneratii*) shell biological membrane have been prepared / isolated as described earlier in the chapter V. The membrane thus obtained were cut into a circular disc form of unit cross-sectional area sealed between two half cells of an electrochemical cell as shown in Fig (7.2).

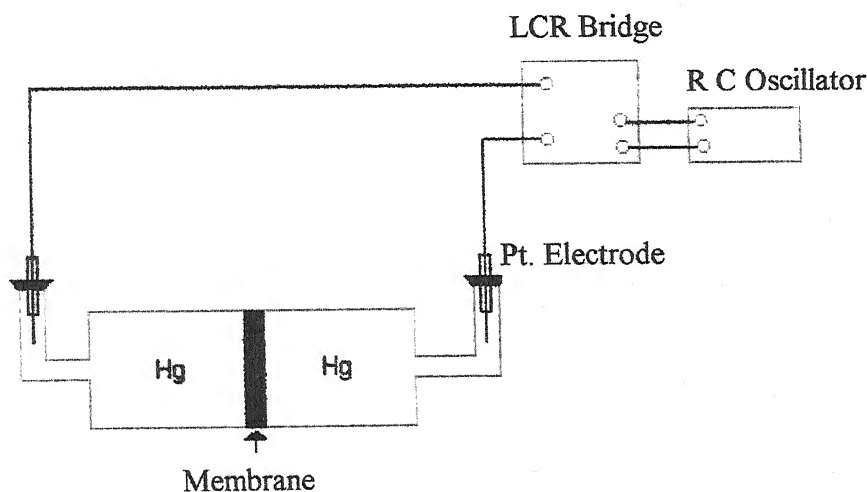


Fig. 7.2

Cell for measuring the membrane resistance and capacitance

The two half cells were first filled with electrolyte solution (sodium chloride) to equilibrate the membranes. The solutions were then replaced by purified mercury without removing the adhering surface liquid⁶⁹ air bubbles, if any, on the surface of the membranes were removed by tilting the cell assembly. Mercury is likely to be oxidised to form mercuric oxide which would form film on membrane faces and cause irreversibility. Use of purified mercury has given reproducible results.

A platinum wire coated with platinum black dipped in mercury was used to establish electrical contacts. The use of long electrode was preferred in order to avoid tip impedance¹⁸. The electrical resistance R_x and capacitance C_x across the membranes were measured by a universal LCR bridge 921 at different frequencies (1, 2.5, 4.0, 5.5, 7, 8.5 and 10 KHz) using RC oscillator 1005. All the measurements were carried out using a water thermostat maintained at $25 \pm 0.1^\circ\text{C}$. The sodium chloride solutions were prepared from analytical grade reagent and deionized water.

Results and Discussion

The values of membrane resistance, R_x , and membrane capacitance, C_x , of parchment supported lead tungstate and hen egg shell membranes bathed in different concentrations of aqueous solutions of sodium chloride and measured at frequencies 1-10 KHz are given in Table 7.1 - 7.4 For comparison these are also depicted in Figs. (7.3-7.10) as a function of concentration and applied frequency. Fig. (4.3) demonstrate that membrane resistance decreases with increase in electrolyte concentration. This behaviour was seen at every frequency and with both the membranes under investigation. The decrease in membrane resistance with increase in electrolyte concentration may be ascribed due to the progressive accumulation of ionic species within the membrane and thus making the membrane more conducting.

Table 7.1

Observed values of membrane resistance, $R_x \times 10^{-2} (\Omega)$ at different frequencies (KHz) for parchment supported lead tungstate membrane equilibrated with different concentrations of sodium chloride solution.

Frequency (KHz)	Concentration (Mol / l)				
	1.0	0.1	0.01	0.001	0.0001
1.0	0.74	1.00	7.40	9.20	12.90
2.5	0.71	0.92	6.20	8.30	11.30
4.0	0.62	0.85	5.30	7.10	9.60
5.5	0.58	0.79	4.40	6.10	8.50
7.0	0.53	0.76	3.80	5.30	7.30
8.5	0.51	0.72	2.80	4.40	6.80
10.0	0.48	0.70	2.00	3.70	6.00

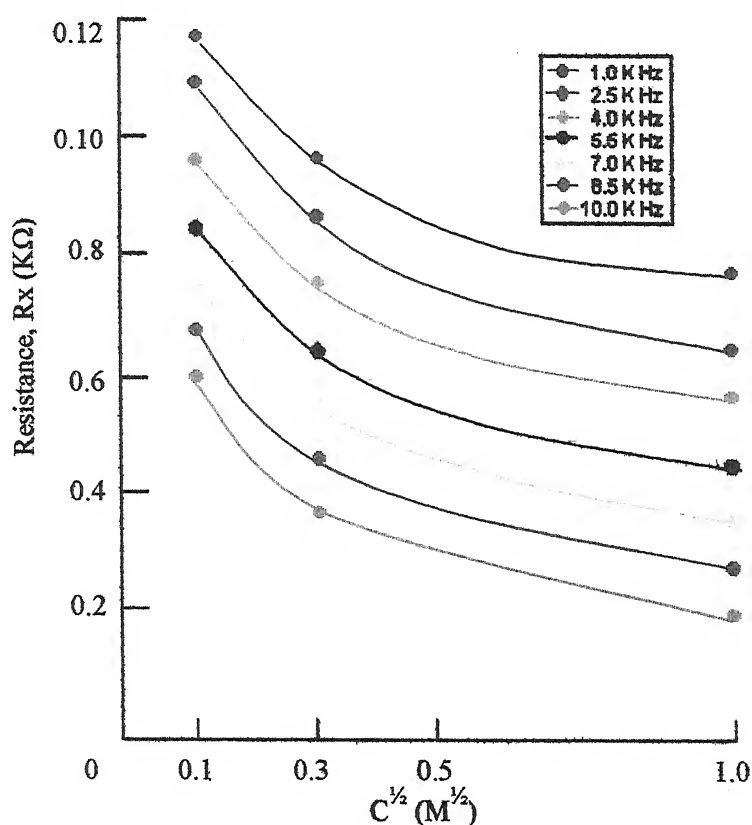


Fig. 7.3

Plots of resistance, R_x (K Ω) against square root of concentrations for NaCl at different frequencies, f (KHz) through lead tungstate membrane

Table 7.2

Observed values of membrane resistance, $R_x \times 10^{-2} (\Omega)$ at different frequencies (KHz) for hen egg shell membrane equilibrated with different concentrations of sodium chloride solution.

Frequency (KHz)	Concentration (Mol / l)				
	1.0	0.1	0.01	0.001	0.0001
1.0	0.46	0.81	3.50	7.10	9.40
2.5	0.32	0.79	3.30	6.80	8.70
4.0	0.28	0.70	2.91	6.10	7.80
5.5	0.22	0.66	2.51	5.60	7.30
7.0	0.20	0.58	2.25	4.80	6.80
8.5	0.49	0.51	1.90	4.40	6.40
10.0	0.18	0.43	1.20	4.00	5.80

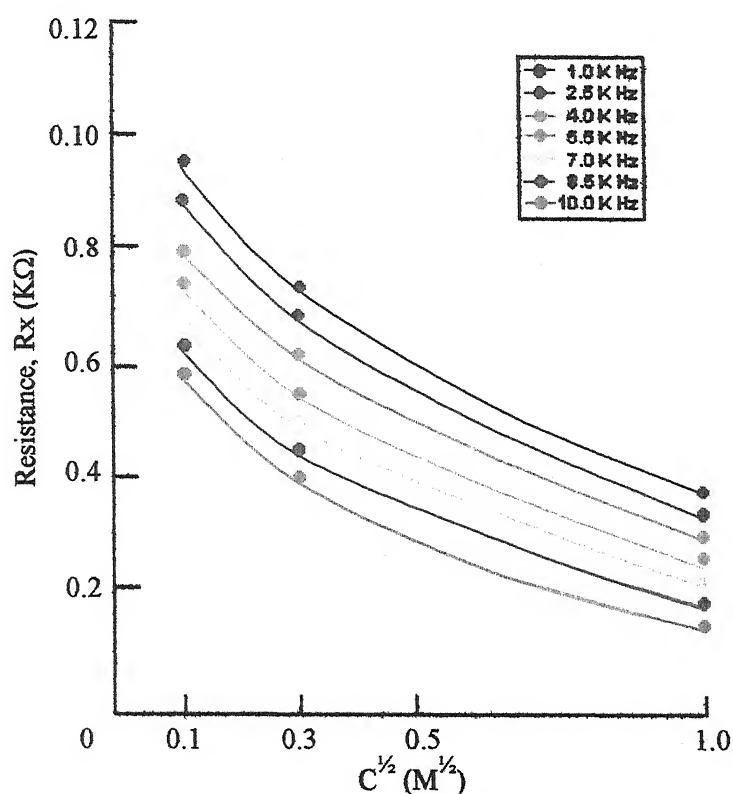


Fig. 7.4

Plots of resistance, R_x (K Ω) against square root of concentrations for NaCl at different frequencies, f (KHz) through hen egg shell membrane

Table 7.3

Observed values of membrane capacitance $C_x \times 10^2$ (μF) at different frequencies (KHz) for parchment supported lead tungstate membrane equilibrated with different concentrations of sodium chloride solution.

Frequency (KHz)	Concentration (Mol / l)				
	1.0	0.1	0.01	0.001	0.0001
1.0	749.0	266.0	78.0	15.9	7.70
2.5	509	180.0	68.5	12.5	6.30
4.0	280.0	136.0	58.0	7.8	4.40
5.5	211.0	114.0	48.0	4.8	3.30
7.0	166.0	98.0	44.6	3.1	2.80
8.5	120.0	96.0	41.8	1.5	0.68
10.0	79.0	71.0	38.0	1.0	0.58

Table 7.4

Observed values of membrane capacitance $C_x \times 10^2$ (μF) at different frequencies (KHz) for parchment supported hen egg shell membrane equilibrated with different concentrations of sodium chloride solution.

Frequency (KHz)	Concentration (Mol / l)				
	1.0	0.1	0.01	0.001	0.0001
1.0	1159.0	462.0	342.0	85.01	5.30
2.5	899.0	280.0	220.0	6.8	3.10
4.0	450.0	162.0	142.0	5.3	2.100
5.5	300.0	75.0	68.0	4.1	1.30
7.0	260.0	51.0	44.0	2.8	1.10
8.5	200.0	34.0	30.0	1.8	0.98
10.0	140.0	20.0	18.0	0.93	0.91

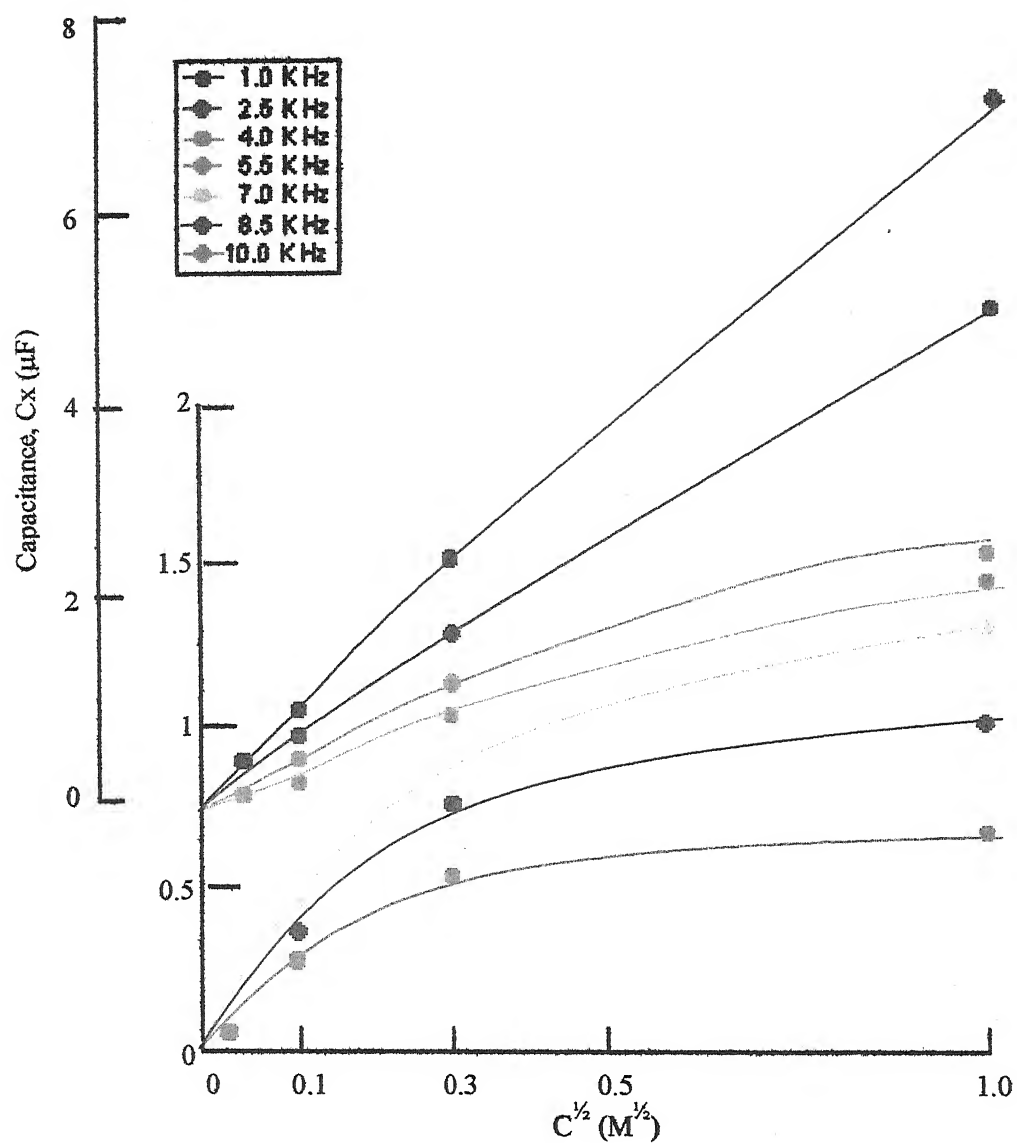


Fig. 7.5

Plots of capacitance, C_x (μF) against square root of concentrations for NaCl at different frequencies, f (KHz) through lead tungstate membrane

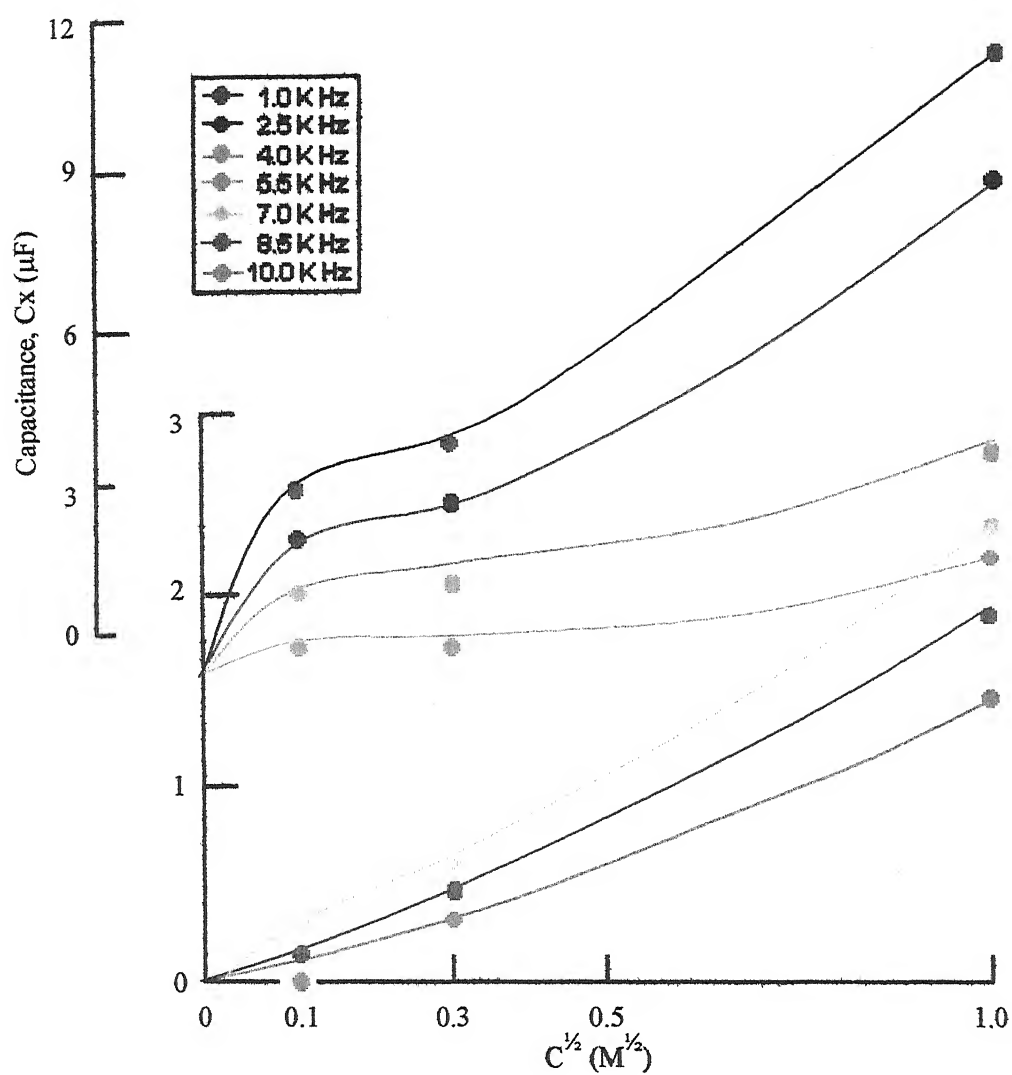


Fig. 7.6

Plots of capacitance, C_x (μF) against square root of concentrations for NaCl at different frequencies, f (KHz) through hen egg shell membrane.

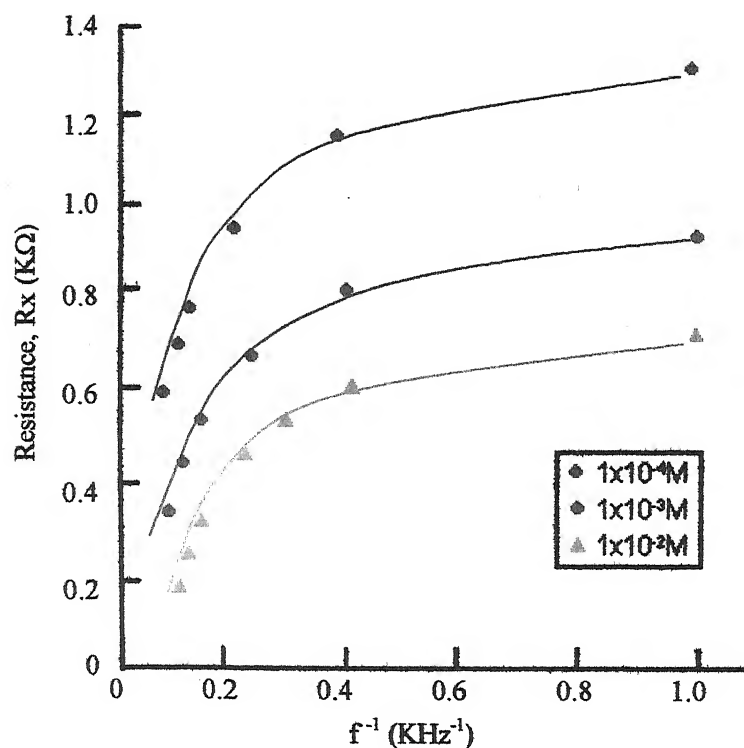


Fig. 7.7

Plots of resistance, R_x ($K\Omega$) against inverse of frequency, f^{-1} (KHz^{-1}) at different concentrations for NaCl through lead tungstate membrane

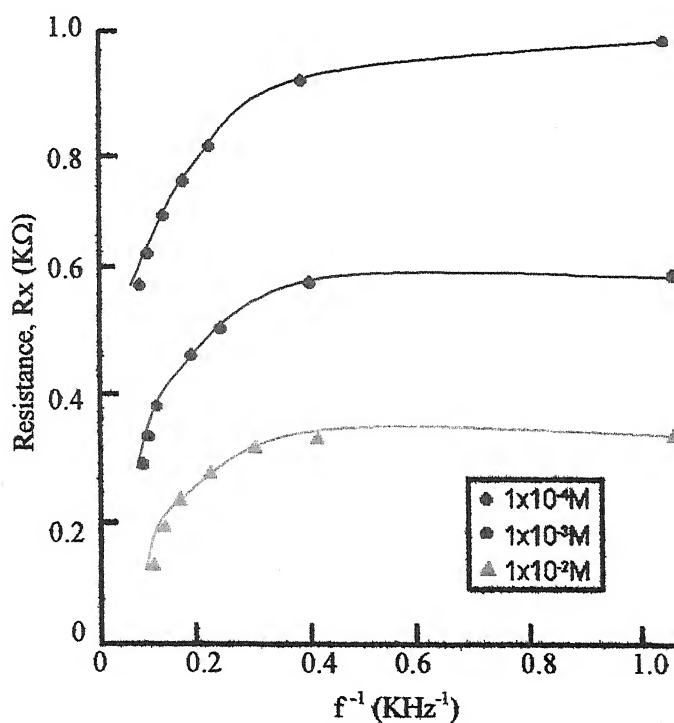


Fig. 7.8

Plots of resistance, R_x ($K\Omega$) against inverse of frequency, f^{-1} (KHz^{-1}) at different concentrations for NaCl through hen egg shell membrane

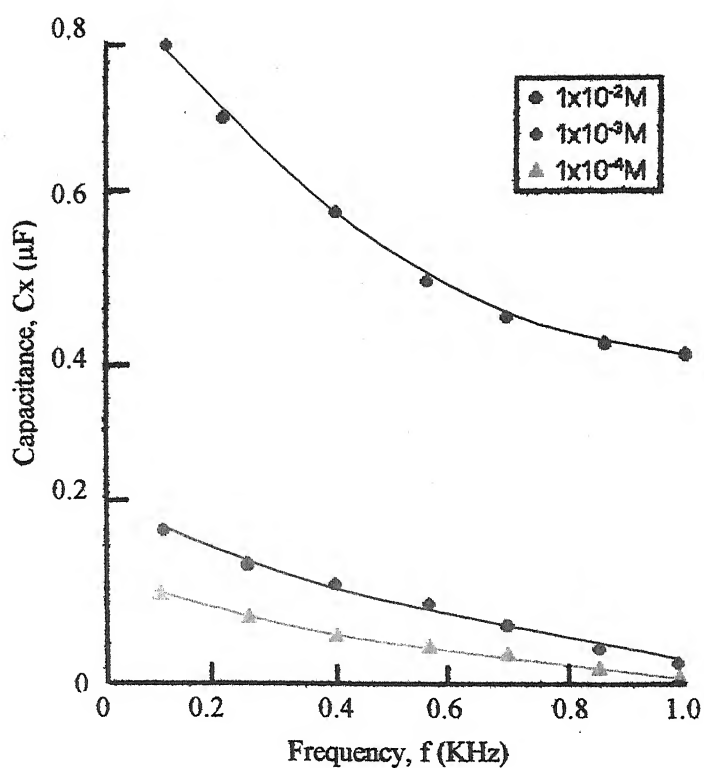


Fig. 7.9

Plots of capacitance, C_x (μF) against frequency, f (KHz) at different concentrations for NaCl through lead tungstate membrane.

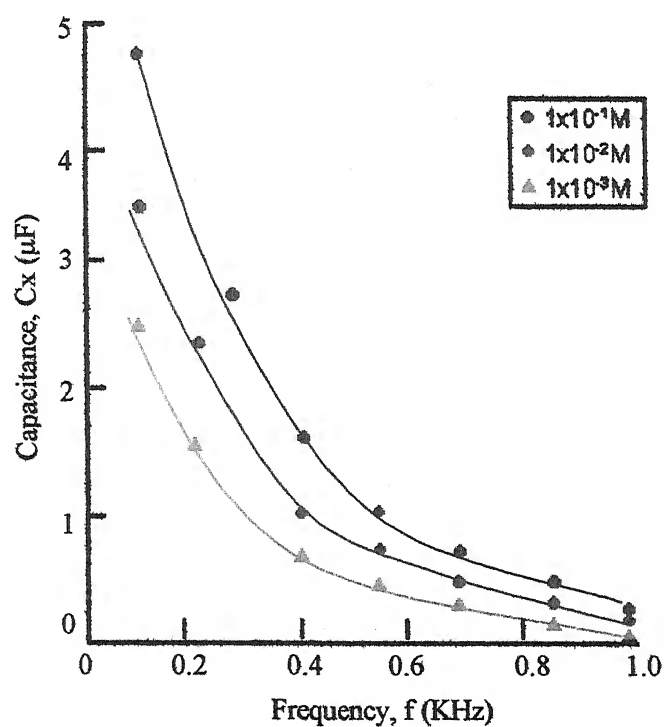


Fig. 7.10

Plots of capacitance, C_x (μF) against frequency, f (KHz) at different concentrations for NaCl through hen egg shell membrane.

On the other hand, membrane capacitance, C_x , increases with the increase in the electrolyte concentrations. This behaviour was seen at each frequency at which measurements were made. The capacitance of a system usually depends upon two factors, viz., directly proportional to dielectric properties and inversely to effective thickness of the capacitor. According to the equation for parallel plate capacitor :

$$C_m = (\epsilon / 36 \times 10^{11} \pi d) \quad (7.1)$$

i.e., membrane capacitance C_m is numerically related to the dielectric constant ϵ , and effective thickness, d , of the membrane. The increase in the value of C_x with electrolyte solution can arise from decrease in the thickness of the membrane or an increase in the dielectric constant of the membrane material or both. Since the species present in the membrane causing this change in C_m are polar in nature (i.e., ion and water), increase in C_m with increase in electrolyte content of the membrane can be attributed to an increase in the values of ϵ . A similar effect of electrolyte concentration on C_m was noted. with thin parlodion membranes by Lakshminarayanaiah and Shanes⁷⁰. Accordingly the increase in membrane capacitance with electrolyte concentration may be attributed to the accumulation of polar substances (ions) within the membrane consequently increase dielectric constant and decrease in the effective thickness of the membrane, most probably due to the de-swelling of the membrane and squeezing of water molecules from the membrane framework by the incoming ions. It may be mentioned here that the effective membrane thickness consists of the membrane matrix and two interfacial surfaces on the two sides of the membrane and that the interfacial thickness controls the membrane phenomena which is electrolyte concentration dependent.

The double layer theory⁷¹ has been utilized in several studies to interpret the changes in the membrane capacitance, C_x , with electrolyte concentrations^{72,73}. C_x is determined primarily by the dielectric constant and the membrane thickness^{74,75}, i.e. by the so called specific geometric capacitance C_g . The

polarization change on the geometric capacitor, in the form of double layer that depends upon electrolyte concentration, plays an important role and affects the overall membrane capacitance C_x . Thus C_g in series with two double layers is given by the expression¹⁶,

$$\frac{1}{C_x} = \frac{1}{C_g} + \frac{2}{C_d} \quad (7.2)$$

here C_d is the capacitance of the interfacial double layer and other symbols have their usual significance. Parchment paper, except for the presence of some stray and end carboxylic acid group, contains very few fixed groups. Deposition of inorganic precipitates gives rise to a net negative charge on the membrane surface in the case of dilute solution of uni-univalent electrolytes leading to the type of ionic distribution associated with water or dilute electrolyte solutions may be assumed to have a constant capacitance, C_g , which may be assumed to depend upon the structural details of the network of which the membranes are composed. The stepwise increase in the membrane capacitance C_x , with the changes made in the electrolyte concentrations may be ascribed to the changes produced in the electrical double layer at the interfaces in the form of interfacial capacitance/capacitor, C_d . In order to analyze the membrane capacitance in terms of geometric capacitance, C_g , and interfacial capacitance, C_d , the observed membrane capacitance in contact with dilute electrolyte solutions was taken equal to the geometric capacitance C_g . This approximation was made due to the fact that membrane capacitance was almost constant particularly in the region of dilute bathing electrolyte solution. Now taking this value of C_x as C_g , the values of C_d at all other electrolyte concentrations were calculated using eqn. (7.2). The values of C_d thus calculated are given in Tables 7.5 and 7.6. The values of C_d decreases (numerically) with increase in the electrolyte concentrations. This confirms our view that effective thickness decreases with increasing electrolyte concentration.

Table 7.5

Calculated values of capacitance of double layer, C_d , at different frequencies (KHz) for parchment supported lead tungstate membrane equilibrated with different concentrations of sodium chloride solution.

Frequency (KHz)	Concentration (Mol / l)				
	1.0	0.1	0.01	0.001	0.0001
1.0	-14.51	-14.82	-15.84	-26.18	-188.00
2.5	-11.911	-12.30	-12.98	-22.48	-161.20
4.0	-8.31	-1.48	-8.83	-18.18	-91.80
5.5	-5.90	-6.04	-6.28	-16.96	-54.08
7.0	-4.88	-4.89	-5.08	-13.51	-31.82
8.5	-0.82	-0.50	-0.50	-0.59	-0.81
10.0	-0.33	-0.32	-0.32	-0.38	-0.44

Table 7.6

Calculated values of capacitance of double layer, C_d , at different frequencies (KHz) for hen egg shell membrane equilibrated with different concentrations of sodium chloride solution.

Frequency (KHz)	Concentration (Mol / l)				
	1.0	0.1	0.01	0.001	0.0001
1.0	-9.60	-9.73	-9.78	-10.18	-127.48
2.5	-5.811	-5.80	-5.87	-10.38	-78.23
4.0	-3.24	-3.28	-3.20	-4.63	-16.13
5.5	-1.56	-1.88	-1.86	-2.31	-5.90
7.0	-1.46	-1.43	-1.42	-1.89	-3.84
8.5	-1.14	-1.16	-1.16	-1.15	-2.89
10.0	-1.00	-1.02	-1.04	-1.23	-2.28

It may also be concluded that the overall membrane capacitance is more dependent upon C_d values which is in agreement with our earlier findings of membrane potential measurements as well as in agreement with Tien and Ting⁷⁶ and Leontiadou et al.⁷⁷ for bilayer lipid membranes (BLM) that the double layers at the interfaces control the diffusion processes. Negative values of C_d may be referred to the opposite polarity of the double layer capacitors connected in series with geometric capacitors, C_g .

The resistance R_x and the reactance X_x of simple membranes are, in general, considered equivalent to the electrical circuit as shown in Fig. (7.11a) and a basic RC circuit, superimposed on an image of a membrane bilayer to show the relationship between the two is shown in Fig. (7.11b).

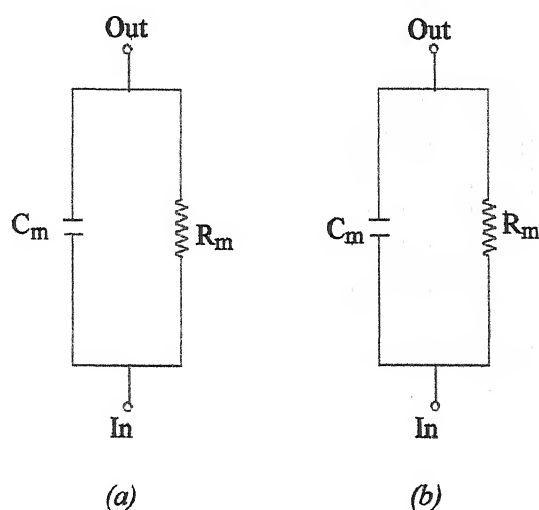


Fig. 7.11

The equivalent electrical RC circuit for (a) The model membrane (b) The biological membrane.

Lakshminarayanaiah and Shanes⁷⁰ have evaluated the membrane resistance R_m and capacitance C_m by the usual analysis from the equations

$$R_m = R_x \left[1 + \left(\frac{X_x}{R_x} \right)^2 \right] \quad (7.3)$$

$$\omega C_m R_m = \frac{X_x}{R_x} \quad \text{or} \quad C_m = \left(\frac{X_x}{R_x} \right) \frac{1}{\omega R_m} \quad (7.4)$$

$$\text{and } X_x = \frac{1}{\omega C_x} \quad (7.5)$$

where $\omega = 2 \pi f$ and f is the frequency (KHz) used to measure C_x and R_x and for the calculation of C_m , R_m and X_x which are given in Tables 7.7 to 7.12 as a function of both external electrolyte concentration and frequency. The impedance Z of a membrane is given by

$$Z = \sqrt{R_x^2 + X_x^2} \quad (7.6)$$

and the values derived for the membranes in equilibrium with different concentration of sodium chloride solution are given in Tables 7.13 and 7.14.

Table 7.7

Values of membrane reactance $X_x \times 10^4$ (Ω) at different frequencies (KHz) for parchment supported lead tungstate membrane equilibrated with different concentrations of sodium chloride solution.

Frequency	Concentration (Mol / l)				
(KHz)	1.0	0.1	0.01	0.001	0.0001
1.0	0.21	0.62	2.02	9.98	20.42
2.5	0.14	0.36	0.91	9.41	10.11
4.0	0.13	0.30	0.68	8.52	8.88
5.5	0.12	0.26	0.59	7.60	8.78
7.0	0.11	0.23	0.53	6.33	8.13
8.5	0.16	0.18	0.44	5.90	7.07
10.0	0.19	0.16	0.43	5.54	6.23

Table 7.8

Calculated values of membrane reactance $X_x \times 10^4 (\Omega)$ at different frequencies (KHz) for parchment supported hen egg shell membrane equilibrated with different concentrations of sodium chloride solution.

Frequency (KHz)	Concentration (Mol / l)				
	1.0	0.1	0.01	0.001	0.0001
1.0	0.14	0.36	4.00	18.8	30.6
2.5	0.06	0.23	2.91	9.6	21.0
4.0	0.07	0.26	2.80	7.5	20.6
5.5	0.08	0.38	2.40	6.0	20.0
7.0	0.09	0.46	1.00	2.8	19.01
8.5	0.09	0.54	0.88	2.3	18.0
10.0	0.112	0.78	0.63	1.8	17.0

Table 7.9

Calculated values of membrane resistance $R_m \times 10^{-2} (\Omega \text{ cm}^2)$ at different frequencies (KHz) for parchment supported lead tungstate membrane equilibrated with different concentrations of sodium chloride solution

Frequency (KHz)	Concentration (Mol / l)				
	1.0	0.1	0.01	0.001	0.0001
1.0	0.82	1.36	7.5	19.8	24.2
2.5	0.73	1.08	6.30	11.41	20.3
4.0	0.63	0.96	5.38	11.09	17.8
5.5	0.60	0.86	4.49	12.80	17.5
7.0	0.58	0.84	3.58	14.30	16.2
8.5	0.56	0.78	3.88	24.61	14.1
10.0	0.54	0.75	2.08	7.3	12.4

Table 7.10

Calculated values of membrane resistance $X_x \times 10^4 (\Omega)$ at different frequencies (KHz) for hen egg shell membrane equilibrated with different concentrations of sodium chloride solution.

Frequency	Concentration (Mol / l)				
(KHz)	1.0	0.1	0.01	0.001	0.0001
1.0	0.48	0.93	3.54	17.2	10.8
2.5	0.36	0.84	3.32	20.5	56.7
4.0	0.38	0.79	2.92	15.7	57.8
5.5	0.27	0.76	2.58	16.5	61.4
7.0	0.24	0.95	2.37	18.2	69.6
8.5	0.22	1.08	2.08	26.8	65.2
10.0	0.25	1.93	1.86	82.1	56.3

Table 7.11

Calculated values of membrane capacitance $C_m \times 10^3 [\mu f (Cm^2)^{-1}]$ at different frequencies (KHz) for parchment supported lead tungstate membrane equilibrated with different concentrations of sodium chloride solution.

Frequency	Concentration (Mol / l)				
(KHz)	1.0	0.1	0.01	0.001	0.0001
1.0	0.56	0.44	0.24	0.08	0.06
2.5	0.28	0.23	0.14	0.16	0.021
4.0	0.25	0.15	0.09	0.05	0.03
5.5	0.15	0.08	0.08	0.021	0.018
7.0	0.12	0.07	0.07	0.018	0.015
8.5	0.11	0.09	0.176	0.008	0.01
10.0	0.10	0.08	0.05	0.032	0.014

Table 7.12

Calculated values of membrane capacitance $C_m \times 10^3$ [$\mu\text{f} (\text{Cm}^2)^{-1}$] at different frequencies (KHz) for hen egg shell membrane equilibrated with different concentrations of sodium chloride solution.

Frequency	Concentration (Mol / l)				
(KHz)	1.0	0.1	0.01	0.001	0.0001
1.0	1.00	0.71	0.50	0.39	0.33
2.5	0.32	0.22	0.18	0.042	0.026
4.0	0.28	0.18	0.96	0.033	0.017
5.5	0.43	0.33	0.14	0.018	0.010
7.0	0.39	0.19	0.048	0.008	0.009
8.5	0.38	0.18	0.04	0.034	0.008
10.0	0.39	0.16	0.045	0.015	0.0073

Table 7.13

Calculated values of membrane impedance $Z \times 10^{-2}$ (Ω) at different frequencies (KHz) for parchment supported lead tungstate membrane equilibrated with different concentrations of sodium chloride solution.

Frequency	Concentration (Mol / l)				
(KHz)	1.0	0.1	0.01	0.001	0.0001
1.0	0.78	1.18	7.78	9.32	24.20
2.5	0.72	0.98	6.36	9.74	20.32
4.0	0.63	0.89	4.35	8.95	13.06
5.5	0.58	0.83	3.45	8.86	12.15
7.0	0.56	0.79	3.53	8.64	10.93
8.5	0.53	0.75	3.84	9.46	9.87
10.0	0.52	0.72	2.05	16.31	8.63

Table 7.14

Calculated values of membrane impedance $Z \times 10^{-2} (\Omega)$ at different frequencies (KHz) for parchment supported hen egg shell membrane equilibrated with different concentrations of sodium chloride solution.

Frequency	Concentration (Mol / l)				
(KHz)	1.0	0.1	0.01	0.001	0.0001
1.0	0.48	0.87	3.54	19.98	32.05
2.5	0.34	0.82	3.32	11.82	22.38
4.0	0.31	0.75	2.92	9.73	21.42
5.5	0.26	0.70	2.55	9.10	23.44
7.0	0.22	0.74	2.32	9.75	21.77
8.5	0.21	0.78	1.18	10.86	20.32
10.0	0.20	0.73	1.97	18.13	18.08

Membranes under investigation possess negatively charge and the counterions form the double layer at the membrane surfaces. By the increase of electrolyte concentration the counterions in the from of double layer are pushed inside the membrane, resulting thereby a decrease in the effective thickness of the membrane and increase in the ionic charge within the membrane. These conclusions support our data on membrane resistance and our earlier findings that the double layer at the interface controls the transport phenomena. Impedance of the system increases with decrease in the electrolyte concentration whereas it decreases insignificantly with the increase in the frequency at which the measurements were made. Thus membranes may be considered to be more effective as barrier when it is separating dilute electrolyte concentration and that at higher concentration the effect of the membrane tend to vanish. These data

again support our findings of membrane potential measurements described in chapter V of this thesis.

A capacitor⁷⁸ fails to present a perfect and constant capacitance due to $I^2 R$ losses in the plates, connecting wires, interfacial polarization and power loss in dielectric etc. which is usually described in terms of loss angle δ . In a perfect capacitor, the phase angle ϕ between current I and voltage V is 90° whereas the decrease in the phase angle represents the imperfectness in the capacitor as shown in Fig. (7.12).

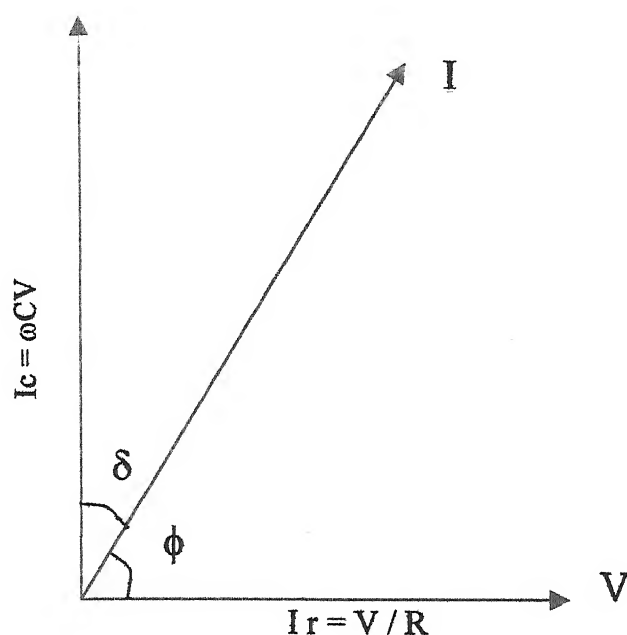


Fig. 7.12

For loss angle δ and phase angle ϕ

For a perfect capacitor $\phi = 90^\circ$ and $\delta = 0$. Loss angle is defined mathematically by the expression.

$$\tan \delta = \frac{1}{\omega C_m R_m} \quad (7.7)$$

where the symbols have their used significance. The loss angle δ calculated at various electrolyte concentrations using equation for the parchment supported lead tungstate and hen egg shell membranes are given in Tables 7.15 and 7.16.

Table 7.15

Values of loss Angle δ of Parchment supported lead tungstate membrane using aqueous sodium chloride solution at different concentrations and frequencies (KHz).

Frequency (KHz)	Concentration (Mol / l)				
	1.0	0.1	0.01	0.001	0.0001
1.0	19°47'	15°13'	8°36'	5°43'	2°55'
2.5	17°44'	14°37'	5°13'	4°3'	1°49'
4.0	16°13'	13°38'	5°17'	5°5'	3°25'
5.5	14°37'	12°55'	4°36'	4°37'	4°6'
7.0	20°19'	19°49'	7°25'	4°48'	4°3'
8.5	18°18'	15°13'	4°47'	4°38'	1°48'
10.0	14°34'	13°30'	10°16'	5°36'	4°7'

Table 7.16

Values of loss Angle δ of hen egg shell membrane using aqueous sodium chloride solution at different concentration and frequencies (KHz).

Frequency (KHz)	Concentration (Mol / l)				
	1.0	0.1	0.01	0.001	0.0001
1.0	17°49'	13°30'	5°43'	4°36'	3°54'
2.5	31°0'	19°48'	6°19'	4°6'	2°18'
4.0	20°24'	24°18'	8°0'	4°5'	2°13'
5.5	15°13'	5°32'	4°36'	5°2'	2°19'
7.0	13°31'	10°48'	9°43'	7°30'	2°6'
8.5	10°48'	3°54'	1°30'	1°13'	1°2'
10.0	9°6'	2°55'	2°13'	1°12'	1°5'

The value of loss angle increases with the increase of electrolyte concentration resulting thereby that capacitors in the form of membrane tend towards imperfectness. This is again in accordance with our conclusions of the impedance determinations. It is quite probable that in these cases the polarization produced at the interfaces in the form of electrical double layer play a dominant role in the diffusion processes.

Conclusion

The impedance characteristics of parchment supported inorganic precipitate lead tungstate model membrane and hen egg shell biological membrane have been analyzed in order to understand the mechanism of ionic diffusion through membranes. The observed values of membrane capacitance and resistance were found to be dependent on the concentration of bathing electrolyte and applied oscillator frequency. The change in membrane capacitance and resistance values with the change in electrolyte concentration and oscillator frequency has been interpreted in terms of changes produced in the electrical double layer at the membrane-solution interface.

This type of behaviour is in agreement with our earlier finding of membrane potential measurements with lead tungstate and hen egg shell membranes as well as in agreement with Tien and Ting for bilayer lipid membranes (BLM) that the electrical layers at the interfaces control the diffusion processes, at least in dilute concentration ranges.

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Chapter – VIII

Future Prospects

Membrane science and technology has come a long way since its origin in the 1960s and is now accepted as a part of available separations technologies in the process industries. But the promise it offers of low cost, highly specific separations has still not been fully realised. Making membrane is still an art rather than science and construction of large scale process plant remains fraught with uncertainty, except in areas such as biotechnology, food processing and water treatment where extensive process know-how has been developed.

Membrane science and engineering have become very successful in developing increasingly economic technologies for the recovery of potable water from seawater and in the purification and disinfection of water. Although there are examples of the successful application of gas membrane technology, it is probably still too early to rank membrane technology alongside more conventional gas processing technologies for large scale use.

Because the world in the 21st century is faced with a number of significant processing challenges and these will require large scale economic operation, it is suggested that the attention of membrane researchers could profitably be directed to these areas. They include separation of CO₂ from the burning of fossil fuels, the provision of adequate quality water for urban environments and the treatment of waste water to protect the environment.

It is appropriate at this time to evaluate where future opportunities lie for membrane technology and where there will be substantial community support for R&D effort. This is not to say that fundamental work should not proceed in the hope of major breakthroughs. But it is fair to comment that we know enough

about membrane science and technology to see where it has optimum application, where new work is needed, and where there are significant opportunities if technological problems can be overcome. There are real lessons to be learned from examining how well the development of membrane technology parallels that of other separation technologies and what have been the principal drivers for significant developments in these technologies.

The principal problems facing the world in this century are :

- (i) The impact of global warming
- (ii) Meeting increasing demands for energy
- (iii) Provision of adequate supplies of water in developed and developing countries
- (iv) Sustainable minerals processing
- (v) Protection of the environment.

Water treatment is one of the great success stories of membrane technology. Reverse osmosis now accounts for half of the installed new capacity for seawater desalination, micro filtration and nanofiltration have both made inroads for the purification and disinfection of drinking water and have replaced more conventional technologies.

The challenges for the membrane industry is to see whether membrane technology can offer the long term solution to the world's water needs, both by supplying an inexpensive process and offering a high degree of reliability. The ultimate challenge is to provide for safe recycle of water, overcoming cultural taboos by technology that satisfies all members of society. What is being talked of is a range of membrane-based plants at a scale hitherto unenvisioned.

Those active in membrane science have probably reflected often on the "ultimate" membrane. This is a membrane that will have a high permeability and bring about the desired separation with a high degree of precision. With such a

membrane, the challenge then becomes one of managing the process conditions on either side of the membrane so that concentration polarization or fouling effects are minimized by good fluid mechanics, chemistry and mass transfer management. The choice of trans-membrane pressure then becomes a question of providing sufficient driving force to attain a desirable permeability.

For membranes designed for liquid phase separations, especially the removal of dissolved and suspended species from water, membrane effectiveness depends on the existence of micron or submicron pores, assisted by local charge to repel ionic species. It still remains unclear what is the primary separation mechanism in tight reverse osmosis membranes.

Conceptually, at least, it should be possible to design a membrane with a very high pure water permeability but at the same time having high rejection capabilities for ionic or non-ionic species. Like a gas separation membrane, this membrane would have zones of molecular dimensions of high permeability surrounded by zones which repelled ionic or charged species and induced a local environment rich in the permeating species. The challenge for the membrane scientist is therefore to develop new membranes based on an understanding of the rejection and transfer characteristics which are sufficiently thin to require a minimum trans membrane pressure to allow them to function effectively.

The ultimate challenge is to design membranes that will operate at high temperatures and have high mechanical stability. Latest generation ceramic membranes offer promise here as they confer the benefit of high permeability and can be aggressively cleaned. It is argued that the real challenges for membrane technology lie in addressing some of the large-scale problems facing society in the next 30 years.

In future, the largest market for membrane will continue to be water treatment, with sales to manufacturers of consumer water purification equipment

becoming more important. In addition, as both the physical and chemical means of cleaning membranes continue to improve, the average life span of the membranes is lengthening, thus reducing replacement sales.

Biomedical applications are by far the most relevant use of synthetic membranes. Membranes are used in medical devices such as hemodialysers, blood oxygenators and controlled drug delivery systems. There is however a substantial effort focused on the development of the membrane for the next generation of artificial organs, such as artificial liver or artificial pancreas. In this device, as in other novel vehicles for the delivery of the cell and gene therapy, synthetic membranes are combined with living cells to form so-called biohybrid organs.

The liquid – liquid electrochemistry to be a versatile tool in the characterization of drug properties with relevance to drug delivery and pharmacokinetics. While the bare interface between two immiscible electrolyte solutions enables the determination of partition coefficients for both the neutral and charged species of ionisable compounds, a.c electrochemical measurements can be combined with theoretical models to reveal the membrane activity of variable classes of therapeutics. The sensitivity of capacitance measurements to detect charges in membrane activity, induced by minor alterations in structure, holds promise for future applications in this field of biosensing.

Membrane technologies continue to offer considerable promise. Perhaps it is time for the membrane research fraternity to examine the future path of the technology and its alignment to major international process challenges where good science and clever engineering can be utilized to produce reliable and economic solutions.

Summary

The steady deteriorating conditions of human life in civilized areas have much diminished the number of those who once considered the chief aim of science to be the unlimited subjugation and transformation of nature. The main importance of science, of course, never lay in this area and in the process of seeking a more thorough understanding of nature. Scientists have constantly imitated nature, especially, living nature. This direction appears even more promising at the present time, since the artificial tools, materials or processes, developed are not only useful in themselves but, in addition provide models which on investigation provide a deeper understanding of the natural phenomena.

Transport phenomena in membrane has acquired considerable significance during the last few decades because of its direct impact in desalination, ion sensor techniques, fuel cell technology nanotechnology, electrical storage batteries, medicine and several other processes. The investigators from various disciplines e.g. chemists, chemical engineers, physicists and biologists have contributed extensively, although the aims and the starting points have been quite different.

The number of recent published research papers and reviews has witnessed a rapid growth in the development and use of model membranes for carrying out investigations of various aspects of bio-electric phenomena. A number of investigators have developed simple, well defined and stable model membranes, lipid bilayer membrane have been considered as the most realistic model except for few shortcomings. Parchment paper, which mimic some of the functional properties of electrolyte cell and gastric mucosal membranes, have been used to study the rectification phenomena in biological systems and in some other physico-chemical studies. Inorganic precipitate membranes, owing to their stability at higher temperatures, ion exchange power and strong adsorption

characteristics have been used in many processes of nuclear and chemical technology and electro synthesis of organic compounds in some non conducting media.

Many of the processes occurring in nature involve membrane transport. Some of the functions performed by such membranes appear to be unique, as well as efficient and it could be possible to prepare synthetic membrane of similar properties. Furthermore, knowledge of synthetic membranes with a view to understand the changes which occur in biological ones is the main interest of the authors. However, the main object is the examination of the extent to which electroanalytical method may be applied to answer the questions concerning the physical chemistry of ion transport across membranes.

Model and biological membranes are studied simultaneously by using the recently developed theories. Biological membranes with the exception of cell membranes, are thin sheets of tissue that cover various organs of body and plants. Of the hundreds of biological membranes, one of the more familiar is the mucous membrane. The mucous membrane functions as a barrier to keep toxic components contacting one side of the membrane from tissue on the other side but allows transport of species essential for that tissue. Model or synthetic membranes are sub-classified by composition, functions, structure and form. Composition refers to the material used to make the membrane i.e., organic or inorganic polymer. Functional classification of membranes includes gas separation, water desalination, dialysis etc. Form denotes whether the membrane is a film hollow fiber tube, or coating.

In this thesis, an effort has been made to characterize the hen egg (*Gallus saneratii*) shell biological membrane and newly developed parchment supported lead tungstate ion exchange model membrane, prepared from inorganic precipitates, when placed in contact with aqueous electrolyte solutions. The

parameters governing membrane phenomena have been derived from membrane potential, bi-ionic potential, membrane conductance and membrane impedance measurements. The thesis has been presented into following chapters. It is based on the more general approach to membrane transport extended using the non equilibrium thermodynamics.

Chapter-I is the general introduction describing the previous studies related to the present work and the history of membrane science and technology, viz. its origin, development and further fragmentation into a highly sophisticated discipline which makes its presence felt in almost every modern and cutting-edge technology, directly affecting the welfare of mankind .

Chapter-II, describe the general purpose of the present work, development, chemical characterization and applications that would be feasible for electrochemical studies.

Chapter-III is devoted to basic properties of model and biological membranes and existing artificial and biomembrane models. This portion also gives an idea about the general structure of the model and biological membranes with the help of Scanning electron microscopy (SEM), Transmission electron microscopy (TEM) and Fourier transform Infrared spectroscopy (FTIR). The investigation reveals that lead tungstate membrane is composed of dense aggregation of smaller particles and formed pores probably with non-linear channel with fully inter connected particles are irregularly condensed and adopt a heterogeneous structure comprising masses of various size. Infrared spectra gives percentage structural probability of many similar compounds.

Hen egg shell membrane has been found to have greater amount of protein studded in the comparatively lesser amount of lipid. In the light of the above it may be hypothesized that a greater part of protein content of the membrane is devoted to pores and channels. Which are a part and parcel in the passage of ions

across the membrane. Thus it is further concluded that lipid content might be providing a framework to the protein which is largely channels and pores. The infrared spectra gives percentage structural probability with similar compounds like N- (Isobutoxymethyl) Acrylamide and chitin.

Chapter-IV depicts the basic theories of membrane phenomena based on the principles of non equilibrium thermodynamics. Electrochemical characterization of membranes is of vital importance from the point of view of determination of their suitability for many applications of practical interest. Electrochemical studies of biological and model membranes are totally based on certain widely accepted theories of non equilibrium thermodynamics. Various theoretical equations have already been derived by various workers in order to evaluate important parameters governing the membrane phenomena regarding their electrochemical characterization. Basically various approaches are taken into account by the author for the establishment of recent theories for membrane potential, bi-ionic potential, membrane impedance etc, which are the based on the experimental measurements for the characterization of the membranes.

In this way this chapter is restricted towards the various approaches as :

I. Irreversible Thermodynamics Approach :

The linear phenomenological analysis is a powerful tool to characterize membrane transport processes on the basis of non equilibrium thermodynamics. A variety of non equilibrium thermodynamic theories on the membrane transport processes have been developed to investigate material transport phenomena arising across membranes. These membrane theories are useful to describe quantitatively the selective transport performance in some particular membrane samples by evaluating the linear phenomenological coefficients from the available experimental data. However, there seem to be some uncertain factors, even now in the generalized correlations of phenomenological coefficients with membrane

properties such as permeability, selectivity, polymeric and charged structures, and phase behaviour of membrane substances. The theory of irreversible thermodynamics processes has been very successful in treating many sorts of irreversible phenomena.

II. Chemical Engineering Approach :

This approach used to describe membrane transport is based on turning the NP equations of motion inside out. These equations, known as Stefan-Maxwell equations, account for the motion of the centre of mass of the membranes system and remove a source of concentration dependence that measures diffusion coefficient will otherwise show when measured in a laboratory co-ordinate system. A characteristic feature of this method, as with the entirely consistent irreversible thermodynamic approach, is the large number of transport parameters which take into account interacting among moving and static components.

III. Activation Barrier Kinetic Approach :

This theory treats transport processes as barrier controlled kinetic events occurring sequentially in space within the membrane. The advantage of the so called kinetic analysis of membrane transport is that it provides an overview without the introduction of specific models for forces and system functions. On the new parameters are introduced and are related to the other better known quantities.

Absolute Reaction Rate theory :

The rate theory describes process of diffusion in the chemical reaction in terms of elementary jumps over energy barriers and can be used to represent the process of permeation in as much detail or with as much accuracy as desired. The permeant encounters energy maxima (barriers) and minima (wells) in its journey from one side of the membrane to the other. The energy maxima represents the energies of the transition states, and diffusion state, these unfavourable loci can be

represented by single jumps over the corresponding barriers. The progress over each barrier is proportional to the number of ions attaining the energy, needed to cross the barrier. In this process, the rate constant k_i for crossing over a barrier was related to standard Gibb's free energy of activation ΔF^* by the appropriate equation.

$$k_i = A_i e^{(-\Delta F^*/RT)}$$

This equation was further extended in terms of activation energy E_a , enthalpy change ΔH^* and the entropy change ΔS^* of activation to calculate the values of these parameters, that is, E_a , ΔH^* and ΔS^* . The size dependence on the magnitude of E_a , ΔF^* and ΔH^* represented that a larger ion was having more difficulty to cross the membrane rather than a small one. This type of variation was explained by considering the precaution of energy peaks and wells and also by comparing the height of energy barrier, that is, the difference between outer wells and peaks.

IV. Phenomenological Equation of Motion Approach :

This widely applied theory of transport is based on the NP flux equation. In its most general form, it is consistent with irreversible thermodynamic flux.

$$I = F \sum_i Z_i \bar{J}_i - \left(\frac{\partial^2 \psi}{\partial x \partial t} \right)$$

Use of NP equations in steady state uniform (constant composition) electrolyte leads to all of the classical transport relations. The most extensive study of techniques, based on Pleijels procedure for integration of the standards NP equation system applicable to liquid junctions and ion - exchange membranes.

V. Membrane Potential :

In living cells an electrical potential difference exists between the cytoplasm and the extra cellular medium, with the inside of the cell being negative with respect to outside. The potential is called resting potential. It may vary considerably between different types of cells, but it is always smaller than 100 mV. The resting potential is caused by the unequal distribution of ions in the inside and outside solutions on both sides of the plasma membrane surrounding the cell. Therefore, the resting potential is also called membrane potential.

It has been recognized that membrane charge and its density are among the most important factors which characterize membranes. Various theoretical approaches have been made to calculate electrical potential across charged membranes. These have been treated on the basis of the idealized theory of TMS and its refinements and the kinetic approach based on the theory of absolute reaction rate.

(i) Teorell- Meyer- Sievers (TMS) Theory :

The earliest efforts towards developing a membrane model was by Michaelis, who considered that the charge on the membrane was due to adsorption of one kind of ion, later Teorell, Meyer and Sievers developed a theory of membrane with charges fixed in the lattice. In the TMS theory there is an equilibrium process at each solution- membrane interface which has formed analogy with the Donnan equilibrium. In addition there is an internal salt diffusion potential which was first represented by the Henderson equation and later by the more nearly correct Planck expression. Further assumptions made are (a) the cation and anion mobilities and fixed charge concentration are constant throughout the membrane phase and are independent of the salt concentration and (b) the transference of water may be neglected.

The important point emerging from the application of TMS theory is that the mobility ratio goes through a change considerable in some cases in the membrane phase. Usually in the case of cation selective membrane (values of \bar{X} high) $(\bar{u}/\bar{v})_{\rightarrow \infty}$ in dilute solutions and only when the membrane is in equilibrium with concentrated solutions does $(\bar{u}/\bar{v}) \rightarrow (u/v)_{\text{solution}}$. In view of this the approach of TMS is unreliable to evaluate charge density \bar{X} for ion-exchange membranes which have a high concentration of \bar{X} as found in this study, due to the fact that the change in the values of the factor (\bar{u}/\bar{v}) is not drastic as it is with membranes of high charge density. The limitations of this conceptually useful theory which has stimulated both theoretical and experimental work, are applicable only to idealized system and this should be borne in mind when it is applied to analyse membrane phenomena.

(ii) Altug and Hair Theory :

Altug and Hair method is principally based on Teorell's model. This alternative method of plotting the membrane potential data may be expected to give \bar{X} values different from those given by TMS method. It is not very realistic to use the solution mobility values for the ratio u/v in the calculations. It is believed that the approach of Altug and Hair may some times overestimated \bar{X} in comparison to TMS method.

(iii) Kobatake and Nagasawa Theory :

In Kobatake's and Nagasawa's method of charge density evaluation, the derivations are based on the thermodynamics of irreversible process which has its own limitations. They have claimed that their data of membrane potential on an oxidized collodion membrane, as well as those of previous workers, are fitted quite accurately by the equation derived by them. They have also stated that no such agreement with experiment was obtained in terms of the earlier theory of

TMS. These theoretical predictions from the Kobatake membrane potential equations are borne out satisfactorily by my experimental results. So it may safely be concluded that Kobatake's and Nagasawa's approaches for charge density evaluation based on thermodynamics of irreversible processes are more accurate as compared to earlier theories of membrane potential.

(iv) Aizawa Theory :

The Aizawa et al. method is an extended form of Nagasawa et al. approaches for charge density evaluation. The Aizawa et al. access is also based on thermodynamics of irreversible processes. This is also a good method for the evaluation of thermodynamically effective fixed charge density.

VI. Bi-Ionic Potential :

A steady electromotive force of a bi-ionic cell containing two electrolytes AX and BX separated by a membrane is called the bi-ionic potential (BIP). This potential is a measure for the selectivity of a membrane for the ions of the same sign and has been the subject of many theoretical and experimental studies. The mathematically rigorous equations were derived on the basis of the thermodynamics of irreversible processes by Scatchard and Helfferich. In their derivations, however, they considered only a perfectly cation selective membrane separating two mixtures of 1:1 electrolyte with a common anion, i.e. neglected the effect of flow of anion of the BIP. Moreover, these types of treatment did not provide information about the actual mechanism which produces observed BIP for the membrane which arises between solutions of an electrolyte of different concentrations separated by a uniform membrane. Teorell-Meyer-Sievers derived a first theoretical equation based on the fixed charge membrane model. Also, Toyoshima integrated flow equations provided by thermodynamics of irreversible processes under the appropriate assumptions for the mobilities and activity coefficients of small ions in the membrane phase to derive an equation for the

membrane potential and found the derived equation agreed with typical experimental data with porous membranes covering wide ranges of concentration of external solutions.

Chapter- V deals with the characterization and evaluation of effective fixed charge density of the lead tungstate parchment supported membrane and hen egg (*Gallus saneratii*) shell biological membrane from membrane potential measurements using various 1:1 electrolyte at different concentrations. The parchment supported membrane was prepared by the method of interaction adopted by Beg et al.. Hen egg shell membrane was separated from freshly laid down hen egg. The following approaches have been utilized for the evaluation of thermodynamically effective fixed charge density of membranes (i) Teorell-Meyer-Sievers (TMS) method, and its modified form by Altug and Hair (ii) the method developed by Kobatake and co-workers (iii) the method of Nagasawa et al. and (iv) Aizawa et al. method based on the principle of nonequilibrium thermodynamics.

The values of membrane potential measured across lead tungstate membrane with the use of chlorides of potassium, sodium and lithium were all positive at lower concentrations, when the membranes were used to separate electrolytes (dilute solution side taken as positive). However, at higher concentration of sodium and lithium chlorides respectively, membrane potential observed were negative. This means that membranes were a little bit anion selective at very higher electrolyte concentration. Moreover, the membrane potential values increase across the lead tungstate membrane with the dilution of electrolyte solutions. The membrane potential values observed across hen egg shell membrane using various 1:1 electrolyte solutions were negative at all concentration which confirms the anion selectivity of the membrane.

For the evaluation of effective fixed charge density, Teorell-Meyer and Sievers (TMS) derived a theoretical equation for membrane potential when a charged membrane separates different concentrations of an electrolyte by considering a diffusion potential within the membrane and two interfacial potentials at the membrane-solution interfaces. The membrane potential equation, thus derived has been generally accepted and widely used for the evaluation of effective fixed charge density and mobility ratio of the ions within the membranes by the plotting method. The method gave quite satisfactory results.

In TMS method and its modified form by Altug and Hair, the values of (a) Donnan potentials π_1 , and π_2 , (b) Diffusion potential $(\phi_2 - \phi_1)$ and (c) Donnan distribution ratios r_1 and r_2 have been calculated and used for charge density evaluation.

In Kobatake et al. method, the most important assumptions are about the activities, a_+ and a_- , of ions in the membrane phase which can be represented by $a_+ = c_-$ and $a_- = c_+$ where c_- is the concentration of the negative ion species. Kobatake's equation contains various parameters namely α , β and \bar{X} which have been evaluated using a model and biological membranes.

The theory of membrane potential developed by Nagasawa et al. and Aizawa et al. based on the thermodynamics of irreversible processes were also applied for the evaluation of thermodynamically effective fixed charge density of the membranes. Comparison between various theories have been discussed in brief. The results of all these investigations show, that the experimentally determined membrane potential data with these systems of membranes, fit quite accurately in the equations of Kobatake, Altug, Nagasawa. and Aizawa. The values of effective fixed charge densities evaluated from different methods gave identical values.

Chapter-VI describes the determination of the selectivity of the membranes for cations by using the values of bi-ionic and conductivity measurements across the parchment supported lead tungstate and hen egg (*Gallus saneratii*) biological membranes for various combinations of 1:1 electrolytes. Moreover, the selectivity of the membranes was determined by three widely used methods namely : bi-ionic method, one-sided addition method and absolute reaction rates method. Bi-ionic method involves the measurements of electrical potential by keeping the same concentration on the two sides of the membrane. Which were measured across the parchment supported lead tungstate membrane and hen egg shell membranes using various concentrations. The intra-membrane permeability ratio of cations were derived using the plotting method. Conductivity of the membranes in contact with single electrolyte were also determined experimentally in order to evaluate selectivity of the membranes using the predetermined values of intra-membrane permeability ratio. The equation for permeability ratio, selectivity constant and the ratio of the individual ionic mobilities derived recently by Sandblom and Eisenman from the macroscopic laws of irreversible thermodynamics was used to evaluate various membrane parameters. It was found that the theoretical and observed values of BIP, are closer to each other thereby confirming the applicability of Toyoshima's equation to this system of model and biological membranes. The selectivity sequence of both the membranes for the cations were of the following order; $K^+ > Na^+ > Li^+$.

In one sided addition method bi-ionic potentials were carried out by keeping the concentration of one of the electrolytes (AX) constant and varying the concentration of other electrolyte (BX) and then by keeping the concentration of electrolyte BX constant and varying that of AX. Utilizing the best equations of Wilson, Wyllie and Ilani and the data of BIP, effective fixed charge density, the evaluated values confirmed the selectivity sequence of membrane alkali metal

ions as : $K^+ > Na^+ > Li^+$, which on the basis of Eisenman-Sherry model of membrane selectivity point towards the weak field strength of the charge groups attached to the membrane matrix. Perfect Donnan exclusion of coions was realized in the dilute limit of the external solution.

In Absolute reaction rates method the selectivity of model ions of the membranes was also tested in terms of the values of various activation parameters like, E_a , ΔF^\ddagger , ΔH^\ddagger and ΔS^\ddagger , which were predicted on the basis of rate theory. The parameters ΔS^\ddagger , the entropy of activation represents the mechanism of ion permeation in terms of electrolyte diffusion with partial immobility causes the selectivity behaviour of membrane of metal ions, the partial mobilities were increasing with increase of density of charge on the permeant. This conclusion was in good agreement with the most recent finding of Marcus, who established that the transitional immobilization of entropy of solvents follow the sequence; $Li^+ > Na^+ > K^+$ resulting in the selectivity sequence of the membranes for alkali metal ions as : $K^+ > Na^+ > Li^+$.

Chapter-VII is related to membrane characterization using impedance measurements of parchment supported lead tungstate model membrane and hen egg (*Gallus saneratii*) shell biological membrane under various conditions of bathing electrolyte concentration and applied oscillator frequency in order to understand the mechanism of ionic transport through these membranes. The results are interpreted in terms of changes produced in the electrical double layer at the membrane/electrolyte interfaces.

A Universal LCR Bridge-921 has been used to measure the electrical resistance (R_x) and capacitance (C_x) across lead tungstate and hen egg shell membranes equilibrated with different concentrations of sodium chloride solution at different frequencies by maintaining the temperature of the system at $25 \pm 0.1^\circ C$. On the basis of these reported experimental data, a comparison of

charge carrier of the membrane has been carried out. Using some simple models of Lakshminarayanaiah and Shane the theoretical values of electrical resistance, capacitance and impedance were determined in the form of R_m , C_m and Z . Thus comparison of experimentally observed and theoretical evaluated values of electrical resistance, and electrical capacitance of the membranes confirm their existence.

The electrical double layer at the membrane/solution interface has been utilized in several studies to account for various membrane behaviour. Here it is considered in the studies of impedance characterization of the membranes. The calculated values of interfacial double layer capacitance of these membranes are in the agreement with my earlier findings of membrane potential measurements with lead tungstate and hen egg shell membranes as well as agreement with Tien and Ting for bilayer lipid membranes that the electrical double layers at that interfaces control the diffusion processes, at least in dilute concentrations ranges

Chapter-VIII highlights the uses of membrane science and technology in various discipline and industries namely, food and biotechnology industries, leather and textile industry, dairy Industry, medical sector, reverse osmosis, bioreactors, biomedical devices and various others.

List of Acronyms

BIP	Bi-ionic Potential
BLM	Bilayer Lipid Membrane
DPPC	Dipalmitoyl Phosphatidyl Choline
DPPS	Dipalmitoyl Phosphatidyl Serine
DSC	Differential Scanning Calorimetry
EDI	Electrodeionization
ESR	Electron Spin Resonance
FTIR	Fourier Transform Infra Red
GC	Goy-Chapman
GCS	Goy-Chapman-stern
IEM	Ion Exchange Membrane
IS	Impedance Spectroscopy
KHz	Kilo Hertz
LB	Langmuir-Blogett
LCR	Inductance capacitance Resistance.
MBR	Membrane Bio Reactor
MD	Molecular Dynamics
MF	Micro Filtration
NF	Nano Filtration
NMR	Nuclear Magnetic Resonance
NP	Nernst-Plank
PB	Poisson-Boltzmann
PC	Phosphatidyl Choline.
PE	Phosphatidyl Ethanolamines

PI	Phosphatidyl Inositols
PMA	Polymethacrylic Acid
PS	Phosphatidyl Serines.
PSA	Phenosulphonic Acid
PSSA	Polystyrene Sulphonic Acid
PV	Pervaporation
RC	Resistance Capacitance.
RO	Reverse Osmosis
SCE	Saturated Calomel electrode
SEM	Scanning Electron Microscopy
SPHM	Sphingomyelins
SWAXS	Small and Wide Angle X-Ray Scattering.
TEM	Transmission Electron Microscopy
TMS	Teorell-Meyer-Siever
TPAs ⁺	Tetra Phenyl Arsonium
TPB	Tetra Phenyl borate
UF	Ultra Filtration
XRD	X-Ray Diffraction

List of Symbols

$C_{i,b}$	Bulk concentration of ionic species
N	Surface density of binding sites.
K_i	Binding constant of ion i
D	Mean diffusion coefficient
nm	Nanometer.
mV	Milivolt.
T	Absolute temperature.
N_A	Avogadro's Number
Z	Charge number
e	Proton charge
\ln	Natural logarithm
X_i	Mole fraction
C_i	Concentration
V_i	Partial molar volume.
J	Flux
P'	Internal permeability
\bar{C}_1	Concentration of first barrier.
\bar{C}_n	Concentration of n th barrier.
\bar{K}	Rate constant
A_i	Frequency
E_a	Energy of Activation
d	Inter ionic jump distance.
E_m	Membrane potential
\bar{u}	Mobility of the cation

\bar{v}	Mobility of the anion
C_1, C_2	Concentrations
E_{cal}	Total membrane potential
r_1, r_2	Donnan distribution ratios
R	Molar gas constant
a	External solution activity.
E	Electrical potential
C_+	Concentration of positive ion
C_-	Concentration of negative ion
U	Molar mobility of cation
V	Molar mobility of anion
U_m	Velocity of local centre of mass
a_+, a_-	Activity of ions.
C_o	Equilibrium concentration
$ E_m^\sigma $	Absolute value of reduced membrane potential.
t_{app}^-	Apparent transference number.
u_j^o	Mobility of ion of ion species j in the bulk solution
U_i	Mobility of ion species i in the membrane
F	Faraday constant.
P_s	Permselectivity
J_s'	Phenomenological coefficient.
\bar{C}_-	Concentration of coions.
d	Thickness of the membrane.
t	Transport number of anion.
J_o	Phenomenological coefficient for water molecular
J_+	Phenomenological coefficient for cation

J	Phenomenological coefficient for anion.
J	Flux of ionic species.
c_p, a_p	Gradient of the electron chemical potential of the anion
J_N	Constant with respect to axial direction
J_p	Constant
u_i^o	Mobility of ion i in free solution
v_i^o	Activity coefficient of ion i in free solution
a_{NP}	Mean activities of the electrolyte NP
K	Baltzman constant, standard rate constant of charge transfer
\bar{X}	Charge on the membrane or effective fixed charge density.
$(a_1^1)_o$	Single ion activities of species in the membrane phase at $X = 0$
$(a_1^1)_L$	Single ion activities of species in the membrane phase at $X = L$
$(\mu_N^o)^m$	Standard chemical potential of cation in the membrane phase.
$(\mu_N^o)^b$	Standard chemical potential of cation in the bulk solution
K	Constant
J_o	Flow of electrolyte in the absence of an external electric field.
\bar{a}_1, \bar{a}_2	Activities of the electrolytes on the two sides of the membrane
r_1, r_2	Distribution ratios
E_d	Diffusion potential
E_l	Electrostatic potential
K_i	Rate constant
h	Plank constant
\bar{m}_i	Steady-state equilibrium concentration of i
\bar{m}_j	Steady-state equilibrium concentration j
K_{ji}	Selectivity const.

R_X	Membrane Resistance.
C_X	Membrane capacitance
C_d	Capacitance of the interfacial double layer
C_m	Calculated membrane capacitance.
X_X	Reactance.
R_∞	High frequency bulk Resistance.
Z_1	Infinite transmission line
Z_2	Finite transmission line
C	Double layer geometric capacitance
C_g	Specific geometric capacitance.
R_m	Calculated membrane resistance.
Z	Membrane impedance.
f	Frequency
E	Electrical potential
U_m	Velocity of local central mass
$(I)c$	Electric current density
X_i	Mole fraction
C_i	Concentration
C_o	Equilibrium Concentration
ψ_o	Surface Potential
ψ_s	Double layer Potential
ψ_d	Dipole potential
$\Delta\psi$	Potential difference.
σ	Surface charge density
σ_a	Surface density of adsorbed charge.
Σ	Electrical permittivity

ΔH^*	Enthalpy of Activation.
ΔF^*	Free energy of Activation
ΔS^*	Entropy of Activation
γ_+	Activity coefficients of positive ion
γ_-	Activity coefficients of negative ion
γ_i^o	Activity coefficient of ion species j in the bulk solution.
γ_i	Activity coefficient of ion species i in the membrane
ϕX	Thermodynamically effective fixed charge density of the membrane.
τ_-	Fixed transference number of anion in the membrane.
$\Delta\phi_{BIP}$	Bi-ionic potential
η	reduced concentration
π	Conductance
$\bar{\lambda}_i$	Conductivity of the membrane when it is wholly in i form
$\bar{\lambda}_j$	Conductivity of the membrane when it is wholly in j form
μF	Micro Farad
ϵ	Dielectric constant.
δ	Loss angle
ϕ	Phase angle
$\phi \epsilon_w$	Dielectric permittivity of water
μ_s'	Chemical potential

List of Publications

Research papers :

1. R.S. Kushwaha, **Mohd. Ayub Ansari**, Naheed Akhtar and P. Singh, Studies of inorganic precipitate membranes: Evaluation of membrane selectivity from bi-ionic potential and conductivity measurements. Ind. J. Chem., Vol 31A, 439-442 (1992).
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 11. **Mohd. Ayub Ansari**, Impedance characteristics of parchment supported lead tungstate model membrane. J. Memb. Sci. & Tech. (Under communication).
 - 12.. **Mohd. Ayub Ansari**, Transport studies with hen egg (*Gallus saneratii*) shell membrane. J. Memb. Biol. (Under communication).
 - 13.. **Mohd. Ayab Ansari**, Studies with inorganic precipitate lead tungstate membrane: Test of various theories in the evaluation of membrane selectivity from electrical potential and conductivity measurements, Bull. Chem. Soc. Jpn. (Under Communication).
 14. **Mohd. Ayub Ansari**, Electrochemical studies on hen egg (*Gallus saneratii*) shell membrane, Bioelectrochemistry (Under Communication).

Abstracts :

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- of Indian Council of Chemists, held at Jammu University, Jammu (J & K) from 24-26 Oct. (1994).
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